Assessing Potential for Movement of Active Substances and their Metabolites to Ground Water in the EU

The Final Report of the Ground Water Work Group of FOCUS
(FOrum for the Co-ordination of pesticide fate models and their USe)

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FOREWORD BY THE FOCUS STEERING COMMITTEE

Since its beginning in 1993, FOCUS (FOrum for the Co-ordination of pesticide fate models and their USe) has established a number of work groups to develop procedures for estimating concentrations of plant protection products and their metabolites in various environmental compartments (ground water, surface water, soil, sediment, and air) and for performing kinetic analyses. The procedures for assessing potential movement to ground water became effective in December 2000 and have been used since then as part of the EU registration process. A few years after the release of the scenarios, scientific progress in the field of leaching models as well as experience with the use of the scenarios resulted in questions being raised regarding changes to the scenarios, harmonization of the different leaching models, the role of more advanced assessment approaches (for example, graphical information systems and non-equilibrium sorption), how to use the results of simulations and experimental studies (lysimeter and field studies) in the assessment, and the coverage of new EU member states by the FOCUS scenarios. Therefore FOCUS established a work group of experts from regulatory authorities, research institutes, and industry to develop revised scenarios and an overall framework for assessing leaching potential. This FOCUS group met as a whole 16 times between February 2004 and June 2008 and also many times in various subgroups. This report is the result of extensive deliberation on the numerous issues that arose after conducting a survey of the opinions of the member states. The output of the work group also includes a completely revised set of models, input and output shells, and scenarios which will become available at the FOCUS web site after approval of this report.

The version control process does not allow access to the models for regulatory use prior to their official release date. Therefore, the FOCUS Steering Committee recommends the revised models can be used for leaching assessments immediately after release, but that registrants may use the models released in 2000 for submissions up to one year following the release of these models on the FOCUS web site.

One of the specific details in the remit of the work group was that the revision of the scenarios would include harmonisation of the models (dispersion length, water balance, etc.). This effort was largely successful and the Steering Committee recommends that the ground water assessments can now be performed with any of the models (PEARL, PELMO, and PRZM) and there is no need to perform the assessments with more than one model.

Table of Contents

6

EXECUTIVE SUMMARY

Why is the work of the FOCUS Ground Water Work Group important?

The EU and national registration processes under Directive 91/414/EEC require the assessment of the potential of an active ingredient and its metabolites to move to ground water. An earlier FOCUS work group developed a series of ground water leaching scenarios, which were the basis for the first tier of the EU assessment procedure beginning in 2000. Since that time a number of questions had arisen concerning these scenarios. Also this earlier work group did not provide overall guidance for higher tiers of the entire assessment scheme (field and monitoring studies, lysimeter studies and higher tier modelling approaches).

The current work group has developed a tiered approach for conducting these assessments, which includes the relative roles of modelling, field experiments, and monitoring and incorporates higher tier modelling approaches such as geographical information systems (GIS) and non-equilibrium sorption.

The work group also has carefully assessed the original scenarios and made changes to harmonize differences between models and to make processes as realistic as possible. For example, soil parameters have been adjusted for two of the original locations, crop kc factors changed for all scenarios, runoff eliminated in all scenarios, and new irrigation schedules generated for all irrigated crops.

Finally the EU has significantly grown in size since the original scenarios were issued in 2000. Therefore, whether new scenarios were required to cover the agricultural areas in the new member states needed to be assessed.

To which registration processes are the recommendations directed?

The remit of the work group included developing guidelines for assessing potential movement to ground water under both the EU and member state registration processes. The revised scenarios are directly applicable to EU registration. Some of member states also use these scenarios in their national registration process or may do so in the future.

What are the objectives of the EU and national ground water assessments?

The assessment objectives are different for EU registration of the active ingredient (placement on Annex I) and product registrations in the member states. Although there is no official ground water decision scheme for Annex I inclusion, the current practice is to demonstrate at least one safe use on a representative crop in a significant area of Europe. For national assessments, all crops and the entire potential use area must be considered. If the compound cannot be used safely throughout the country, then the registration may be limited to the subset of conditions under which the compound can be used safely.

What are the desired characteristics of the ground water assessment scheme?

The FOCUS work group objective was to develop a scheme in which the initial (or earlier) tiers are quick, simple, and cheap to undertake and allow the compounds that clearly do not cause any concern to be passed. Conceptually earlier tiers are more conservative than later tiers, which is ensured by the choice of validated models (default assumptions) and choice of parameters (laboratory) and conservative nature of the scenarios in earlier tiers. The later (or higher) tiers are more complex and expensive but should provide a more realistic (less conservative) result. Therefore, results of higher tier assessments supersede results from lower tier assessments.

What is the work group proposing as a ground water assessment scheme?

The work group proposes the following basic scheme with four tiers. This tiered approach is applicable to both EU and member state evaluations, even though the objectives are different.

Where there are a number of options for a given tier, undertaking all options is not necessary. Any single option is sufficient. However, any approaches should be justified using all appropriate data available.

Tier 1	**1)** Standard scenarios with lab or field degradation data

| Tier 2 | **2a)** Modelling with refined parameters | **2b)** Modelling with refined scenarios |

| Tier 3 | **3a)** Combined modelling refined parameters & scenarios | **3b)** Advanced spatial modelling | **3c)** Higher tier leaching experiments set into context by modelling | **3d)** Other modelling approaches |

| Tier 4 | **4)** Ground water monitoring |

* Mitigation possible at all tiers
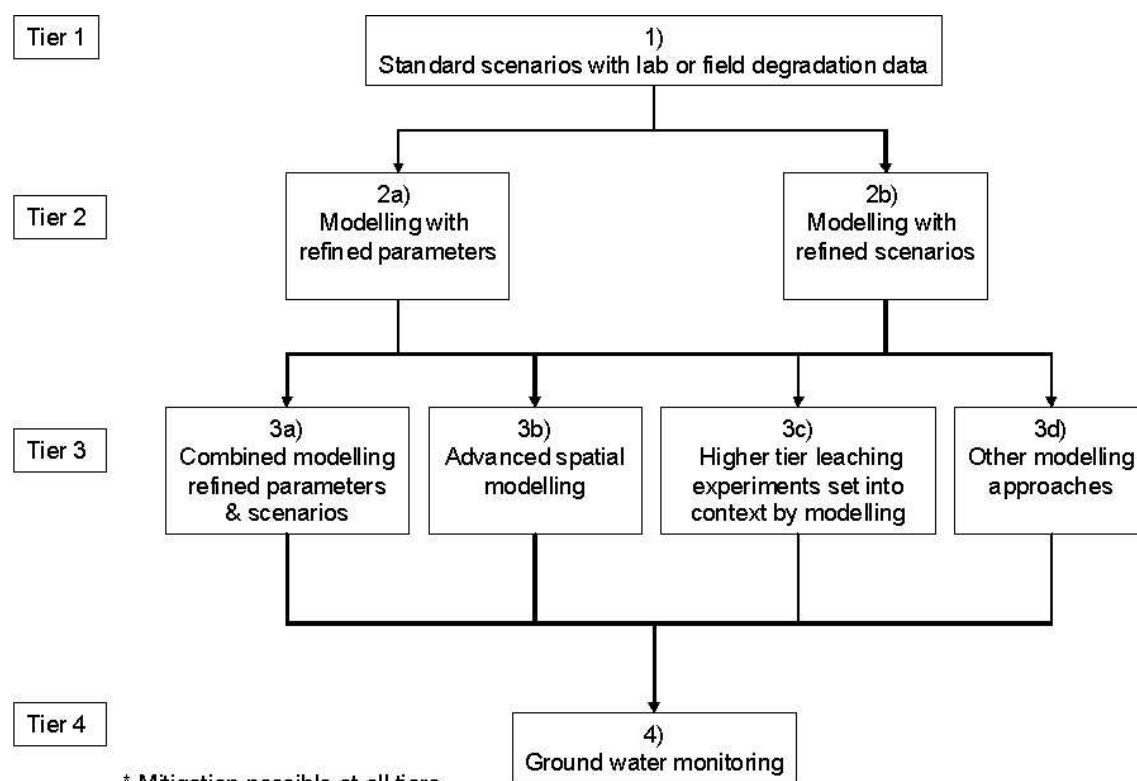
Proposed Generic Tiered Assessment Scheme for Ground Water

Tier 1

Tier 1 in the EU consists of the FOCUS 2000 standard scenarios, which will eventually be replaced by revised scenarios developed by the current work group. In the member state evaluations, a subset of the FOCUS standard scenarios or national scenarios are used. Degradation rates may be from either laboratory or normalised degradation rates from field dissipation studies.

Tier 2

Tier 2 consists of more refined modelling approaches. Tier 2a consists of modelling with refined parameters. This includes providing data on specific processes (for example, sub-surface degradation or non-equilibrium sorption) or particular conditions (such as soil-specific degradation rates) relevant to a particular crop or member state. Tier 2b consists of modelling with refined scenarios. This approach is appropriate when the standard Tier 1 scenarios are not representative of a specific crop or use area. The work group report presents two different methods in detail for determining refined scenarios.

Tier 3

Tier 3 consists of four options consisting of different modelling approaches and modelling combined with experiments. When relevant to the proposed use pattern, Tier 3a combines the refinements detailed in Tiers 2a and 2b to provide an assessment based on both approaches. In Tier 3b spatially-distributed leaching models provide the user with maps of the predicted leaching concentrations in the intended use area or in a climatic zone. Frequency distributions and percentiles of the leaching concentration can be directly inferred from these maps. The quality of such assessments is very much dependent on the quality and coverage of the underlying soil profile and climatic information. Currently the uncertainty of the soil profile information on a European scale is too high for detailed EU-wide assessments. However, in some countries high quality data are available. Any of the FOCUS models could be incorporated into a spatially distributed modelling framework. Tier 3c combines information from experimental studies such as lysimeter experiments and field leaching studies. While field study measurements do not have the limitation of the assumptions used in leaching models, the results may only be directly relevant to the climatic, pedological and agronomic (crop, timing, application rate etc) conditions in which the studies were conducted. The work group recommends that lysimeter studies be incorporated into the assessment scheme by using inverse modelling to develop estimates of input parameters such as degradation rates and sorption constants. The parameters are then combined with measurements from other sources (for example, for degradation rates the lysimeter results are averaged with a weight of three with the results of field dissipation studies). Then the standard scenarios are re-run with the revised parameter. Tier 3d includes other modelling approaches (for example, stochastic and 3-D modelling). At this time the view of the FOCUS work group is that other modelling approaches are not sufficiently developed for regulatory use at a high tier of the risk assessment scheme. However the work group expects that the science will develop in the future and that current research applications may, in time be usable for regulatory purposes.

Tier 4

Tier 4 consists of ground water monitoring data. Ground water monitoring data are seen as the highest tier of assessment since the actual concentrations in ground water are directly measured rather than being estimated by modelling approaches or approximated from small scale lysimeter or field studies. For existing pesticides monitoring data can be useful at both the EU level and the national level. For instance, representative data from one member state could demonstrate a "safe use" for the EU evaluation. For new active substances historical

monitoring data are clearly not available, but post-registration monitoring programs may be possible. Monitoring data can include the results of dedicated analyses of ground water by notifiers or other agencies (i.e. water companies, environment agencies etc) where there may be a detailed initial assessment of the relevance of the monitoring points (for example, by knowledge of historical compound usage in the area and characteristics of the aquifer) and certain minimum quality criteria are demonstrated.

Mitigation

At any tier of the assessment process, mitigation (measures taken to adjust or restrict the use of a pesticide to reduce the risk of leaching to an acceptable level) is possible. Mitigation measures often relate to the Good Agricultural Practice (GAP), and include crops to which a compound can be applied, the timing/crop stage for uses on each specific crop, the application rate, the number of applications, and the timing between applications. Other potential mitigation measures include preventing applications on soils with certain properties (through soil or geographical restrictions), restricting applications in hydrogeologically vulnerable areas, and limiting applications to certain times of the year.

How have the Tier 1 scenarios been revised?

The revisions to the scenarios consisted of:
- Changes to the soil profiles in Porto and Piacenza
- A new procedure for calculating the leaching concentration (PECgw)
- Source of potential reference evaporation data for five locations
- Adding irrigation to some crops grown in Porto.
- Harmonisation between models
  - Harmonisation of the dispersion length
  - Limiting the maximum rooting depth to 1 m
  - Implementation of common crop kc factors for different crop periods
  - Standardising the prediction of evaporation from bare soil
  - Harmonising runoff by eliminating runoff in Tier 1 scenarios
  - Generating crop specific irrigation schedules with PEARL and PELMO

What was the basis for the changes to the soils properties for Porto and Piacenza?

At the time that the FOCUS 2000 scenarios were established, there was a lack of high quality and harmonised EU-wide data bases. For this reason, the original scenarios were selected by a combination of approaches including expert judgement, locations in major agricultural

areas, and distribution of sites to cover all European climatic zones. Research conducted after the issuing of the original scenarios indicated that scenarios at Piacenza and Porto may not have met the desired vulnerability criteria for leaching. To revise the scenarios, the current work group had to decide the precise vulnerability criteria for revision of these scenarios. The criterion selected was the 80th percentile soil and 80th percentile weather for the climatic zone represented by the respective locations. The climatic zone was defined on the basis of the EU area with 15 member states so that the addition of member states did not require the whole set of scenarios to be revised. In addition, the basic spatial unit for leaching was defined as the soil mapping unit and the basic temporal unit was an annual average for annual applications.

What were the changes to the soil properties for Porto and Piacenza?

A spatial analysis of the climatic zones represented by the Porto and Piacenza locations indicated that a change in the organic matter was appropriate to make them fit the vulnerability concept. The organic matter in the surface soil at Porto was decreased from 6.6 to 2.45 percent, resulting in changes to the bulk density, hydraulic properties, and the organic matter in the deeper soil layers. The organic matter in the surface soil at Piacenza was increased from 1.72 to 2.17 percent, along with changes to the organic matter in the deeper soil layers.

How is the weather percentile for PECgw determined?

The previous FOCUS work group decided that the PECgw corresponding to a reasonable worst case for leaching assessments would be approximated by an 80th percentile soil and an 80th percentile weather. The current work group also reviewed several approaches for determining specific percentile values and decided that the 80th percentile weather is represented by the average of the 16th and 17th of the 20 ranked values from the simulation. In the previous Tier 1 scenarios, the 17th ranked value was used. For applications made every second or third year, FOCUS 2000 calculated the flux weighted averages for each of the 20 two or three year periods and then selected the 80th percentile of these 20 values. The current work group investigated taking the 80th percentile of the 40 or 60 yearly values. Because the two methods gave similar results, the work group recommended continuing with calculating the 80th percentile of the 20 flux weighted averages.

Why was harmonisation of the dispersion length important and how was this done?

In simulations conducted according to the procedures in the previous FOCUS work group PEARL and MACRO used a dispersion length of 5 cm and the effective dispersion length

(set by compartment size) in PRZM and PELMO was 2.5 cm. Later work showed that the difference in dispersion lengths was a major source of the difference between predictions of PEARL and PELMO or PRZM. Work group members undertook several activities associated with dispersion. First, a data base of dispersion lengths reported in the literature was derived. This review demonstrated that dispersion increases with depth. Second, changes in how the dispersion process is modelled in a soil profile with depth dependent sorption and decay factors resulted in different predictions of pesticide concentrations at the bottom of the soil profile, even when the different models predicted the same breakthrough of an inert tracer. The pesticide fate models use a one-dimensional convection dispersion equation to describe transport and two options to parameterise this model were discussed. The first option assumes a constant dispersion in the entire soil profile, thereby overestimating the leaching through the upper soil layer where most decay takes place. The second option divided the upper meter in three layers (corresponding to the three different default degradation factors) with increasing dispersion lengths as a function of depth, but the validity of the process description in this approach was questioned. The work group could not come to a consensus over which of the two approaches was preferable. However, because of the need for harmonisation, the constant CDE approach with a dispersion length of 5 cm will be used in the revised scenarios produced by the work group. The constant CDE approach is the more conservative of the two approaches, at least for parent compounds.

What changes were made to harmonise the water balance predicted by the models?

Examination of these differences led to the identification of work in six areas:
- the most appropriate source of reference evapotranspiration data
- the importance of time varying crop kc values
- adjustment of rooting depths
- calculating evaporation from bare soil
- determining appropriate amounts of runoff for each location/crop location and how to achieve this with the different models
- and developing appropriate irrigation files for each location/crop location in the locations where irrigation is a common agricultural practice

Source of reference evapotranspiration data

FOCUS 2000 scenarios used reference evapotranspiration calculated from the MARS data base and FAO crop coefficients. The work group examined whether FAO or MARS referenced evapotranspiration was most appropriate. The work group decided to use FAO reference evapotranspiration for Porto, Piacenza, Châteaudun, Thiva, and Sevilla for consistency between the crop coefficients and evapotranspiration values. The MARS

approach to calculating reference evapotranspiration was retained for Okehampton, Kremsmünster, Hamburg and Jokoinen because there was little difference between the two approaches for these climatic conditions and the long wave radiation parameterisation procedure proposed by the FAO sometimes leads to negative reference evapotranspiration rates in northern European conditions.

Crop kc factors

A comparison of the annual potential evapotranspiration for crop and soil showed that the different procedures within the models for implementing crop kc factors were contributing significantly to the variability of the overall water balance. Therefore the work group decided to harmonize the procedures by implementing a common procedure in which the year was divided into four periods (harvest to emergence, emergence to maturity, maturity to senescence, and senescence to harvest) and a constant kc factor was assigned to each of the four periods. Changes have been made to the models and shells to implement this procedure.

Adjustment of rooting depths

Because transpiration in PEARL is reduced when a substantial fraction of the roots are located below the water table and because of the inconsistency of evaluating ground water concentrations at a depth shallower than the root zone, the work group decided that the maximum rooting depth would not exceed 1 m for all location/crop combinations.

Evaporation from bare soil

In the absence of a crop, evaporation from bare soil is predicted differently in the different models. The procedure used in PEARL was used as the standard and the depth of evaporation parameter in PELMO and PRZM has been adjusted to give approximately the same amount of soil evaporation during the time the crop is not present.

Runoff

Because the work group was unable to obtain a set of crop specific European-wide data to use as a reference for setting runoff amounts that would correspond to an agreed upon percentile for all soils in each FOCUS climate zone, the work group decided to make the conservative assumption of no runoff in PELMO and PRZM and to use the 24 hour storm duration for PEARL in the Tier 1 simulations, which leads to almost no runoff in this model as well. The work group recommends that runoff should be included in Tiers 2b and 3 in EU evaluations and in simulations at the member state level when information on runoff amounts is available.

Irrigation

The work group decided that irrigation schedules should be developed for individual crops in Châteaudun, Piacenza, Porto, Seville, and Thiva because the current irrigation schedules were not always consistent with the cropping season. These irrigation schedules provide irrigation from the time of planting until senescence and are generated using irrigation routines in PEARL and PELMO, which apply irrigation once a week on a fixed day to bring the root zone up to field capacity. However, irrigation was applied only if the amount required exceeded 15 mm. Because of minor differences remaining in the water balance (primarily evapotranspiration), the irrigation routines for PEARL and PELMO predict somewhat different amounts. However, using different irrigation routines tends to compensate for evapotranspiration differences to provide closer estimates between the two models for the amount of water moving below the root zone, which is the key water balance parameter affecting leaching. The irrigation amounts generated by PELMO are used directly in PRZM.

How are these changes being implemented in MACRO?

In 2009 the work group will work with the developers of MACRO to implement equivalent changes in the MACRO Châteaudun scenarios.

How do predictions from the original and revised scenarios compare?

The changes to the models were successful in reducing the variability between the predictions of the models. The following graphs show the comparison of PEARL and PELMO results for compound D between the FOCUS 2000 scenarios and those proposed in this report (FOCUS 2009).
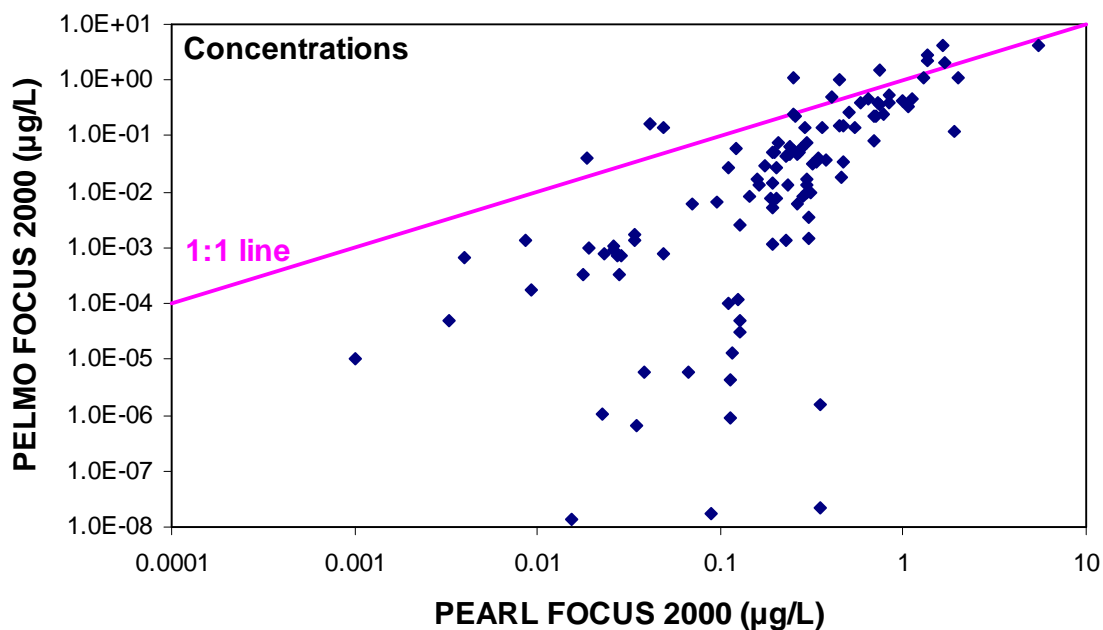
Comparison of the PECgw predicted by PEARL and PELMO for all 125 FOCUS 2000 scenarios.
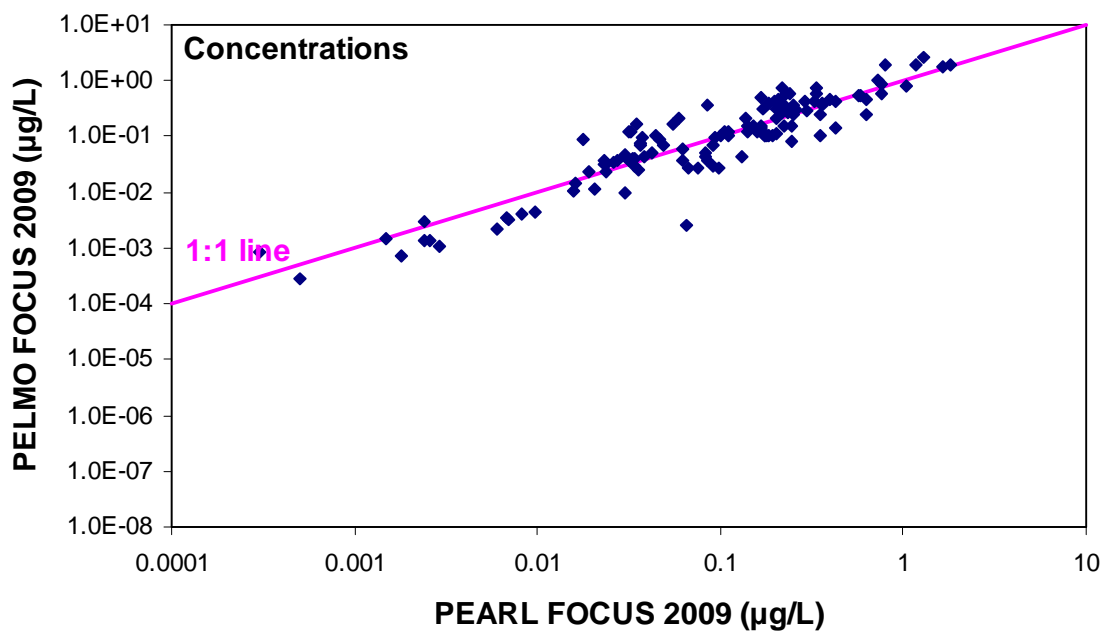
Comparison of the PECgw predicted by PEARL and PELMO for all 125 FOCUS 2009 scenarios.

Each of the changes discussed resulted in changes to the relevant scenarios. For example, the change in calculating the 80th percentile weather lowered concentrations for all 125 scenarios, the changes in the soil properties at Porto increased concentrations for scenarios

at this location (especially for winter crops), and the change in the soil properties at Piacenza reduced concentrations for scenarios at this location. As shown in the following graphs, overall the concentrations predicted by PEARL were generally lower, while the concentrations predicted by PELMO and PRZM increased.
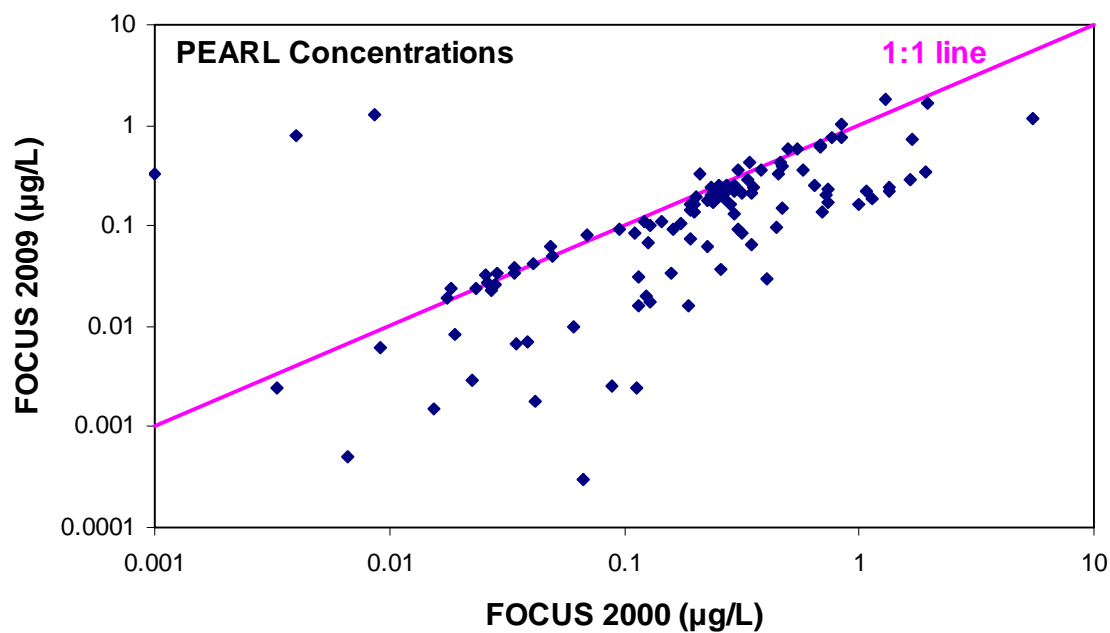
Comparison of the PECgw predicted by PEARL for all 125 FOCUS 2000 and FOCUS 2009 scenarios.
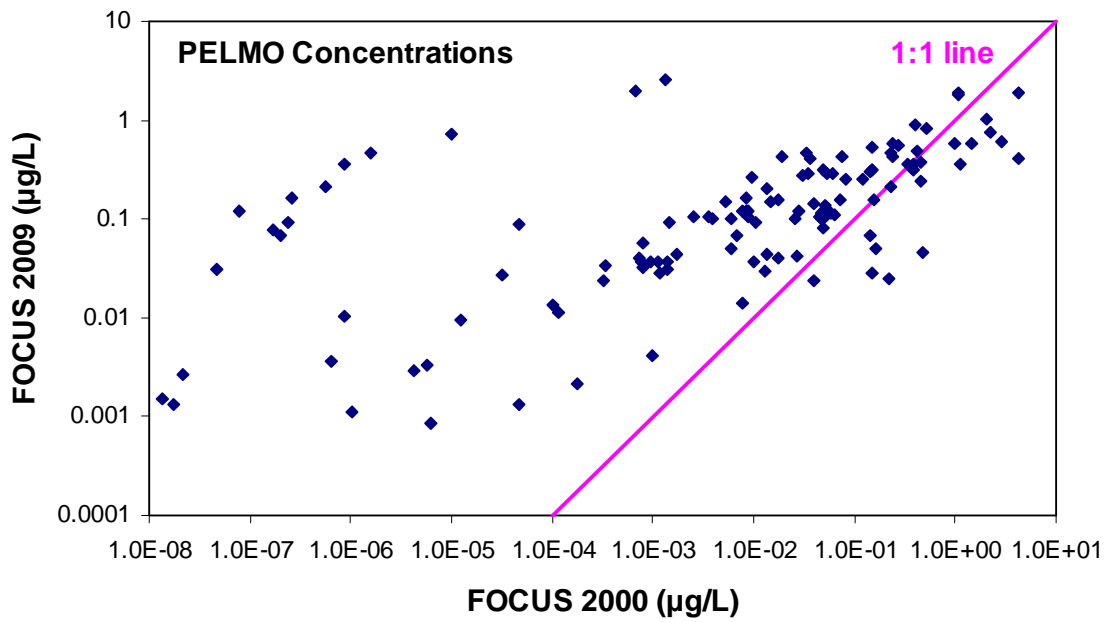
Comparison of the PECgw predicted by PELMO for the 125 FOCUS 2000 and FOCUS 2009 scenarios.
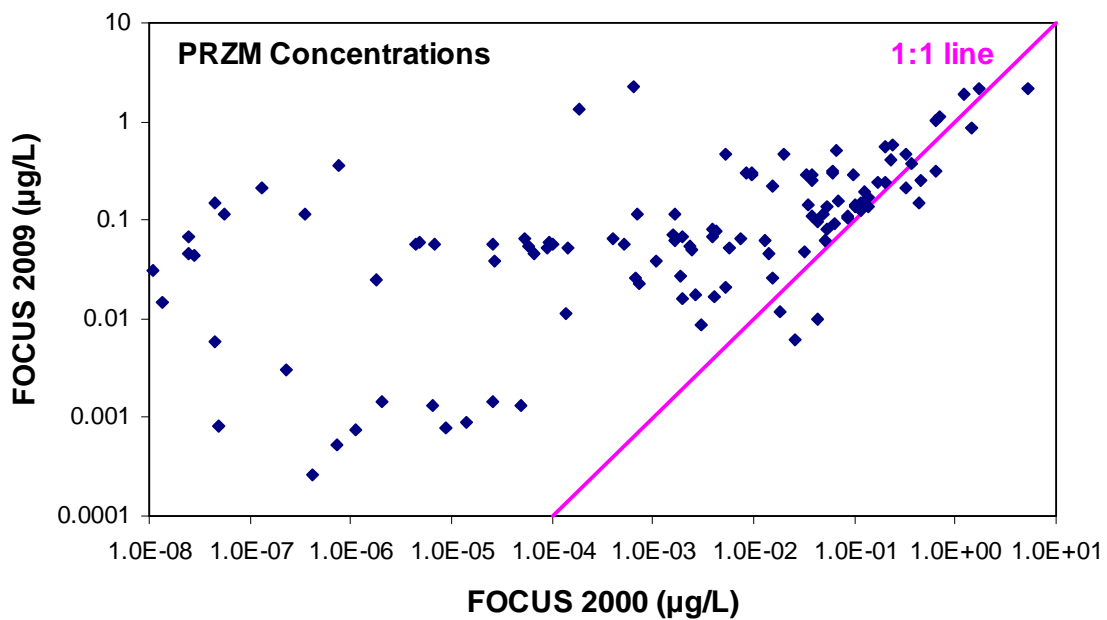
Comparison of the PECgw predicted by PRZM for the 125 FOCUS 2000 and FOCUS 2009 scenarios.

The harmonisation effort was largely successful with 90 percent of the PEARL and PELMO values for the proposed scenarios within a factor of three. This compares to less than one-

fourth of the FOCUS 2000 scenarios. Given the current agreement among the models, the work group recommends that the ground water assessments can now be performed with any of the models (PEARL, PELMO, and PRZM) and there is no need to perform the assessments with more than one model.

Have higher tier modelling approaches been incorporated into the recommendations?

The work group report outlines the principles for spatially distributed modelling and as mentioned earlier presents two different GIS based approaches for creating crop specific scenarios. The work group report provides information on European-wide data sets that could be useful in performing GIS analyses. The report also discusses several approaches, including a detailed discussion of inverse modelling, that combine the results of both field or lysimeter studies with modelling. The work group report also presents a detailed discussion of non-equilibrium sorption, including recommendations for implementation in regulatory submissions.

Have higher tier experimental data been incorporated into the recommendations?

The work group report discusses the design of lysimeter studies, field leaching studies, and ground water monitoring studies and their role in a tiered assessment procedure.

Are the existing scenarios applicable to the new member states?

The FOCUS (2000) scenarios were developed when the European Union consisted of 15 countries. Since that time twelve additional countries have joined. Therefore the work group assessed whether the FOCUS (2000) scenarios 'covers' the agricultural area of new member states. A scenario 'covers' an area when it represents either the same properties or represents a more vulnerable situation like higher rainfall amounts or lower organic carbon contents. The spatial analysis shows that the current set of FOCUS leaching scenarios is applicable to new member countries for the purpose of Tier 1 screening simulations. Some smaller areas shown in the figure below, located both in the original 15 member states and in the newer twelve member states are not covered by current scenario properties. Note that in the figure, Sweden and Cyprus are indicated as not being used for arable land because the Corine Land Cover included no information for these countries at the time this map was produced. In a number of areas shown as not being used for arable land, there are areas of arable land but the resolution and size of the map is not sufficient to indicate these areas.

The areas indicated as not covered by any scenario are not necessarily more vulnerable than covered areas. For example, the not covered areas in central Spain are the result of low organic matter soils. However, these regions are generally of low vulnerability due to hot temperatures and low rainfall.
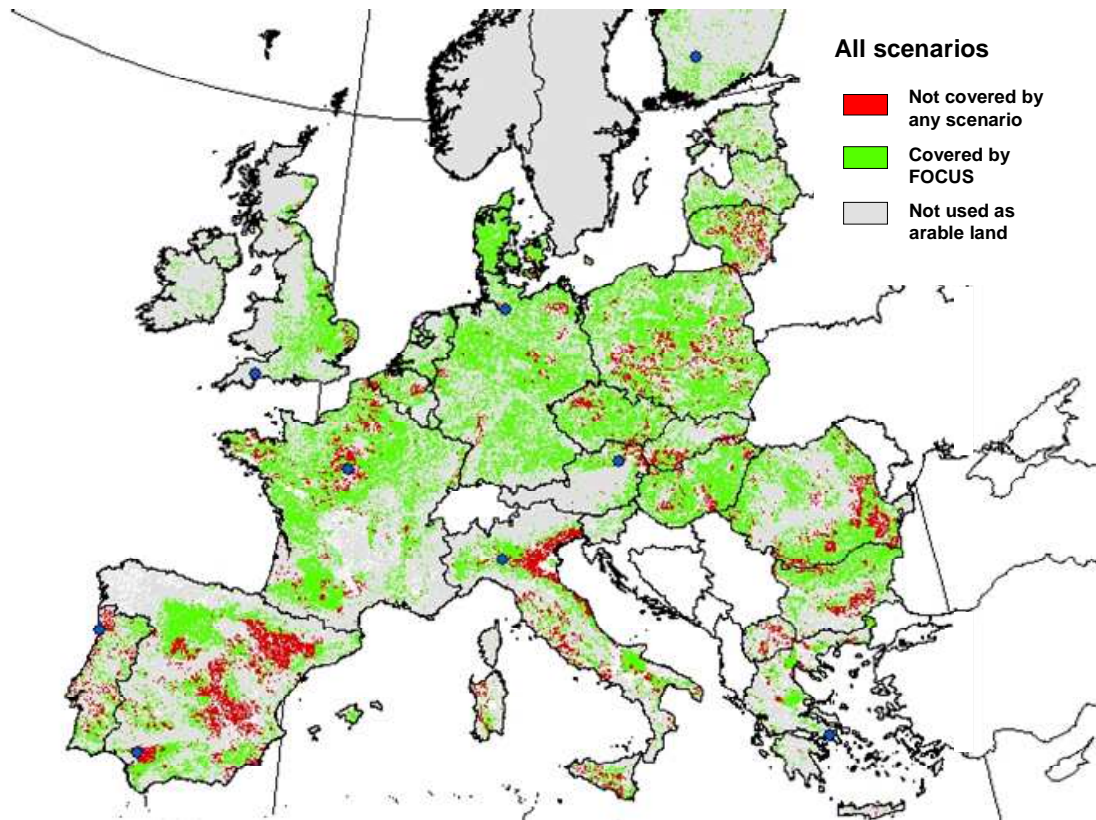
Spatial Analysis of the Coverage of the FOCUS Ground Water Scenarios. In this figure arable land includes orchards, olives, and vineyards.

1   INTRODUCTION

FOCUS (FOrum for the Co-ordination of pesticide fate models and their USe) was a group of regulators, industry, and experts from government research institutes established in 1993 to provide guidance for modelling issues in the rapidly developing EU registration process. FOCUS has sponsored work groups to develop registration guidance in assessing pesticide residues in ground water, soil, surface water, and air.

In the area of ground water, FOCUS sponsored two work groups prior to the work of the current work group, which is described in this report. The first work group reviewed leaching models available for conducting leaching assessments and provided information and guidance on the key issues (FOCUS, 1995). Then FOCUS sponsored a work group to develop standard scenarios for conducting leaching assessments (FOCUS, 2000).

During the years following the release of the original scenarios, a number of questions arose concerning these FOCUS scenarios and issues regarding ground water assessments. While FOCUS (2000) provided a procedure for conducting modelling assessments, this group did not provide overall guidance on the respective roles for field and monitoring studies, lysimeter studies, and modelling for the EU assessment process. In addition member states had adopted significantly different approaches with regards to modelling and studies. Differences between the various models, while acknowledged at the time of the release of the scenarios, became more of an issue, especially differences in the dispersion lengths used and the differences in the predicted water balances. An assessment by APECOP (Vanclooster et al., 2003) challenged the appropriateness of some of the scenarios. The use of higher tier assessment procedures including GIS techniques was becoming more widespread due to increased availability of data and the role of such techniques in the EU assessment process needed to be defined. Finally, the number of countries in the EU was in the process of expanding and the question arose whether additional scenarios would be needed.

FOCUS established a new work group to deal with the questions in the previous paragraph. The work group's remit covered the following four areas:
   a) Develop a sequence of tiers to assess the risk for leaching to ground water in the EU, considering results from different study types (including recommendations for national approaches).

b) Provide a revised set of scenarios and leaching models. This task included the re-evaluation of the Porto and Piacenza scenarios, and harmonisation of the dispersion length and water balance among the models.
c) Develop guidance on the principles for higher tier leaching modelling approaches considering GIS based approaches, the combination of modelling approaches with experimental studies, and inclusion of relevant processes that have been ignored so far.
d) Provide a preliminary assessment of possibilities for scenarios for new member states.

The recommendations of the work group on the tiered assessment scheme are found in Chapters 3-10. The revised scenarios and harmonised leaching models are provided in Chapters 11 and 12. The guidance for higher tier approaches including the combination of modelling approaches with experimental studies has been included in the discussion on the tiered assessment scheme. The applicability of the current scenarios to the new member states is presented in Chapter 13.

When the work group started the EU consisted of 25 member states. During the course of the work, two additional states were added. The work of this work group was based on these 25 member states. However, the EU-wide maps in Chapter 13 do include information from these two new member states.

During the time the work group was preparing this report, the EU Directive 2006/118/EC on the protection of groundwater against pollution and deterioration (European Union, 2006) was issued. The work in this report does not conflict with the EU directive, although in some cases terminology and objectives may be slightly different, especially as regarding ground water monitoring.

1.1 References

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2   GLOSSARY

APECOP

A European Union funded project covering a range of topics associated with modelling the movement and degradation of pesticides in soil.

Chromatographic Flow

Flow of water and solutes through soil that follows the classical convection dispersion equation, with no preferential flow paths bypassing portions of the water filled pore volume.

Crop kc Factors

The crop kc factor times the reference evapotranspiration for a specific day determines the potential evapotranspiration for a specific crop. The actual evapotranspiration for the day may be less, for example due to soil moisture constraints.

DT50, DegT50

DT50 is the time required for 50 percent of the substance to disappear from a compartment. DegT50 is the time required for 50 percent of the substance to disappear from a compartment due to degradation alone. DT50 values may include losses due to volatilisation, leaching, and runoff, while DegT50 does not. In laboratory studies, the DegT50 is usually equal to the measured DT50. If degradation follows singe first order kinetics, then the DegT50 is equal to the half life.

Equilibrium Sorption

In this report, equilibrium sorption is defined as the sorption measured after shaking a batch system for 24 h.

Evapotranspiration

Evapotranspiration is the sum of water losses due to evaporation from the soil surface and transpiration from plants. Evapotranspiration can be either potential (what would occur if the soil was maintained at field capacity) or actual. Reference evapotranspiration refers to potential losses at standard conditions (usually bare soil or a grassed field for a soil maintained at field capacity) and potential crop evapotranspiration refers to potential losses for a specific crop with the soil maintained at field capacity.

Field Capacity

In the FOCUS scenarios, the field capacity is defined as the water content at a tension of 10 kPa (pF2).

Field leaching studies

Studies in which ground water and/or pore water is sampled from a small number of locations following documented application of the pesticide of interest as part of the study. Sites are generally subject to detailed data gathering over a period of months/years. This information would typically include hydrological information (e.g. daily meteorological data, water tensions at different soil depths) as well as additional pesticide information (e.g. bulk soil concentration of pesticide at different depths).

FIFRA

Federal Insecticide, Fungicide, and Rodenticide Act, the primary law providing the legal basis for regulation of pesticides in the United States.

GIS

Geographical Information System, the presentation and organization of information based on location.

GLEAMS

GLEAMS (groundwater loading effects of agricultural management systems) is a one-dimensional leaching and runoff model developed by the U.S. Department of Agricultural.

Guideline Scenarios

Scenarios that are defined in guidelines for higher tier leaching experiments.

HYPRES

A data base of hydraulic properties of European soils.

Inverse Modelling

A modelling technique in which what is normally output information from a model data is used to estimate what are normally input values. For example, using measurements of concentrations as a function of time to estimate sorption constants and degradation rates.

Linear Models

A model F(x) where F is the model operator and x is a variable, is called a linear model when $F(ax+by) = aF(x)+bF(y)$. For example, the model relating the sorption constant, k_d, and the

organic carbon content (OC) is a linear model: $k_d = k_{oc}$ OC whereby k_{oc} is the proportionality factor. Another example of a linear model is a transport model of which the parameters are not a function of the dependent variable, in this case the concentration. For instance, if the gas-water and water-solid partitioning coefficients, and the sorption rate and decay rate parameters are not a function of the concentration, then none of the parameters of the transport model depends on the concentration and the transport model is a linear model. A consequence of this linearity is that the predicted concentrations by the model scale linearly with the applied concentration at the soil surface. Leaching estimates in PELMO, PEARL, PRZM, and MACRO are non-linear due to the use of the Freundlich isotherm

Lysimeter

A lysimeter is a device to sample pore water in soil either at a specific depth or moving past a specific depth. The term can be misleading since there are at least three different devices referred to as lysimeters and all three devices can be used in experiments investigating the movement of solutes in soil.

A soil *monolith lysimeter* consists of a soil block or cylinder, embedded in an inert container (e.g. stainless or galvanised steel, fibre glass) with a bottom permeable to drainage water or leachate (e.g. a perforated bottom, quartz sand filter bottom). See also OECD (2000).[1]

A *zero-tension* lysimeter consists of a permeable bottom plate with simulated water table at that depth.

A soil *suction lysimeter* is a device that draws soil pore water from a specific point in the soil.

MACRO

MACRO is a one dimensional leaching model, which includes the process of macropore flow that was developed at the Swedish University of Agricultural Sciences, Uppsala. MACRO is one of four models used to evaluate potential movement to ground water in the EU registration process.

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[1] OECD (2000) Guidance Document for the Performance Of Out-door Monolith Lysimeter Studies.- OECD Environmental Health and Safety Publications; Series on Testing and Assessment; No. 22.

Macropore Flow

A preferential flow mechanism in which a portion of the water and dissolved solutes bypasses the major part of the soil pore water, without mixing with it, by flowing through cracks or channels in the soil.

Major Metabolite

A degradation product that is formed in amounts of greater a trigger level of 10 % (molar fractions or percent applied radioactivity) of the applied amount of active ingredient at any time evaluated during the degradation studies in the compartment (i.e. soil, water and/or sediment) under consideration.

In the context of the guidance document on relevant metabolites in groundwater (Sanco/221/2000 –rev.10 (25 February 2003)) degradation products must be characterised and identified to the extent that is technically feasible and their relevance must be assessed, if one of the following conditions applies:

a) Metabolites, which account for more than 10 % of the amount of active substance added in soil at any time during the studies; or

b) which account for more than 5 % of the amount of active substance added in soil in at least two sequential measurements during the studies; or

c) for which at the end of soil degradation studies the maximum of formation is not yet reached.

Map Unit

Units with particular characteristics of which the geographical distribution is indicated on a map.

Monitoring Studies

In this report, monitoring studies are studies in which ground water is sampled from a large number of locations in a region or country and is subsequently analysed to determine the concentration of the pesticide of interest. Experimentally determining the reason for the presence or absence of the compound is not necessarily an intrinsic part of these studies, although the weight which is placed on the findings will depend on the appropriate selection of the sites to sample. Outside this report, the definition of monitoring studies is sometimes expanded to include field leaching studies.

pdf

When used in the text, this is an abbreviation for probability density function. When this is part of an electronic file name, this refers to a file that can be read using Adobe Acrobat.

OCTOP

A spatial data base providing information on organic carbon content in European soils.

PEARL

PEARL (Pesticide Emission Assessment at Regional and Local scales) is a one dimensional leaching model developed by three Dutch institutes (ALTERRA, RIVM, and PBL). PEARL is one of four models used to evaluate potential movement to ground water in the EU registration process.

Pedologic

Relating to soil profiles or properties of soil profiles.

PELMO

PELMO (PEsticide Leaching MOdel) is a one dimensional leaching and runoff model developed by the Fraunhofer-Institut für Umweltchemie und Ökotoxikologie. PELMO is one of four models used to evaluate potential movement to ground water in the EU registration process.

Preferential Flow

Flow of water and solutes in soil that does not follow the classical convection dispersion equation, which can result from soil inhomogeneity and channels such as cracks and worm holes. Macropore flow, finger flow, and funnel flow are all preferential flow mechanisms.

PRZM

PRZM (Pesticide Root Zone Model) is a one dimensional leaching and runoff model developed by the U.S. Environmental Protection Agency. PRZM is one of four models used to evaluate potential movement to ground water in the EU registration process.

PSD

Pesticides Safety Directorate, the former government agency regulating pesticides in the United Kingdom (now Chemicals Regulation Directorate).

Reference Scenarios

Scenarios that meet the vulnerability criteria, and define the conditions at which the protection goal has to be met for a favourable regulatory decision. On the EU level, the

reference scenarios are the FOCUS scenarios. At the nation level, the reference scenarios are either national scenarios or specific FOCUS scenarios selected by the member state (see also scenarios).

Relevant Metabolite

In the context of ground water, the term "relevant metabolite" is used in a unique legislative context determined according to Sanco/221/2000-rev. 10 (25 February 2003) and refers to metabolites for which there is reason to assume that it has comparable biological activity as the parent substance or meets certain toxicological properties.

Runoff

Runoff is a term that has been used in the scientific literature in different ways. In pesticide risk assessment, runoff often refers to the flow of water on top of the soil, or alternately overland flow. The most important processes leading to overland flow is infiltration excess runoff (also called Hortonian runoff). Catchment hydrologists commonly use a broader definition of (storm) runoff. They include all processes leading to fast stream response (i.e. infiltration excess runoff, saturation excess runoff from partial contributing areas and subsurface drainage through either artificial drains or naturally occurring preferential pathways). In this report, runoff is used as a synonym for overland flow when referring to Tier 1 scenarios, but can be used in a broader context in Tier 2 and Tier 3.

Scenarios

A representative combination of crop, soil, climate, and agronomic parameters to be used in modelling. There are 125 scenarios in FOCUS 2000 and proposed in this report.

Society of Environmental Toxicology and Chemistry (SETAC)

A profession society dealing with exposure and effects of chemicals in the environment.

Spatially-distributed Modelling

Modelling that is based on running a large number of scenarios with input parameters relevant to specific locations and presenting the results in a map.

STU

Soil Typological Units, which are the carriers of basic soil information, such as the FAO soil name and the soil textural class. Soil mapping units are associations of dominant and subdominant STU's.

Study Scenarios

These scenarios consist of the soil, climatic, and agronomic conditions occurring in a specific higher tier leaching experiment.

Subsoils

Those soil layers located below the plough layer or the surface soil. Typically such soils begin at 0.2 to 0.3 m below the soil surface and continue until the depth of the water table. In some cases subsoils also include layers below the water table, but this is not the case for the usage in this report.

Tiered Assessment Procedure

A sequential assessment procedure with different levels (tiers), in which assessments at a higher level of the procedure will replace assessments at a lower level.

UBA

Umweltbundesamt (Federal Environment Agency), the German government agency responsible for assessing the impact of plant protection products on the environment.

Undisturbed Soil Monolith

An undisturbed soil profile that has been sampled from the field in its original layering of soil horizons without artificial disturbance (no re-filling).

Validated Model

A model which has gone successfully through a validation process for a specified range of validity; this implies that the number of data sets considered is sufficient for the intended use of the model.

Validation Process

Comparison of model output with data independently derived from experiments or observations of the environment; this implies that none of the input parameters is obtained via calibration with the data set used for validation; note that this definition does not specify any correspondence between model output and measured.

Wilting Point

In the FOCUS scenarios, the wilting capacity is defined as the water content at a tension of 16,000 kPa.

3   INTRODUCTION TO ASSESSMENT SCHEMES FOR PEC IN GROUND WATER

3.1   Objectives of the risk assessment for ground water contamination at EU and national levels

The objectives of the risk assessment for ground water contamination has to be considered in the context of the 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 which states (C.2.5.1.2):

No authorization shall be granted if the concentration of the active substance or of relevant metabolites, degradation or reaction products in groundwater, may be expected to exceed, as a result of use of the plant protection product under the proposed conditions of use, the lower of the following limit values:

(i)   the maximum permissible concentration laid down by Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption, or

(ii)   the maximum concentration laid down by the Commission when including the active substance in Annex I, on the basis of appropriate data, in particular toxicological data, or, where the concentration has not been laid down, the concentration corresponding to one tenth of the ADI laid down when the active substance was included in Annex I

unless it is scientifically demonstrated that under relevant field conditions the lower concentration is not exceeded.

A definition of the relevant metabolites is given in the European guidance document SANCO/221.

The Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of ground water against pollution and deterioration has been published recently European Union (2006). The objectives for monitoring under this directive differ from the aspects considered in this report (see Chapter 9).

3.1.1 European level

With regard to ground water contamination no official decision scheme for Annex I inclusion of active substances currently exists. The current practice is to propose Annex I inclusion as far as safe use is demonstrated for a relevant crop and a significant area in Europe. This can be achieved by means of the official FOCUS models and the European scenarios, which were set up to describe realistic worst-case conditions, with an overall vulnerability of the 90th percentile, approximated by using a 80th percentile value for soil and a 80th percentile value for weather (FOCUS, 2000). The current FOCUS group believes that a 90th percentile is consistent with definitions used in the FOCUS 2000 report (this was agreed by the FOCUS Steering Committee and later by the WG Pesticides Legislation). Experimental data (lysimeter, field studies…) can also be provided as supportive information or to refine the assessment.

3.1.2 National level

National risk assessment has to consider the whole area where a PPP is intended to be used, as realistically as possible. The goal is to demonstrate that a compound can be used safely for most of the relevant environmental conditions (at this level it is thought that not all detailed conditions can be taken into consideration). If this conclusion cannot be reached, unfavourable conditions should be identified and risk management may be considered. So, a key point is to know if authorization may be granted only for certain conditions (certain areas, e.g. climatic zones, or certain factors, e.g. soil pH or clay content) or in other words if risk management may be proposed for ground water.

A working definition of the National protection aim was considered by FOCUS to be a prerequisite for definitions of interactions between EU and national assessment schemes.

The proposal of FOCUS is that a national protection goal upper limit should be 0.1 µg/L annual average[2] in ground water at the 90th percentile vulnerability taking into account both spatial variability for soil and climatic conditions, and temporal variability on a multi-year basis, in the agricultural use area of the product. The agricultural use area is defined by the notifier by the intended use. Particular attention would have to be given to areas of higher vulnerability within the agricultural area of the member state that can be identified (e.g. based on defined geographical boundaries or environmental parameters). For these areas, suitable mitigation measures would have to be taken.

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[2] FOCUS criteria for averaging is applied for modelling; see individual subchapters for averaging experimental data.

3.2 Review of existing guidance on EU and national level

3.2.1 Guidance given in EU and FOCUS documents

There are currently a number of publications providing both regulatory requirements and guidance that have relevance for undertaking ground water assessments under Directive 91/414/EEC. These documents refer to both active substances and their metabolites or just to the metabolites. Those that relate to soil degradation aspects have recently been summarised in other FOCUS work (FOCUS, 2006). However, because the degradation requirements are only one aspect of the ground water assessment, a useful starting point for the current FOCUS work group is to summarise the existing information as it relates to all aspects of ground water assessment.

There are two types of publications; EU directives which are considered to be legally binding and Guidance documents which, though highly influential, have no mandatory basis. These are distinguished in the following summary.

3.2.1.1 Binding requirements in directives

The Uniform principles (Directive 97/57/EC establishing the Annex VI to Directive 91/414/EC) require that member states "estimate, using a suitable calculation model validated at the Community level[3], the concentration of the active substance and of relevant metabolites, degradation and reaction products that could be expected in the groundwater in the area of envisaged use…..This evaluation will also take into consideration….the specific information on the fate and behaviour in soil and water as provided for in Annex II"

The decision-making section of Annex VI to Directive 91/414/EC goes on to state that no authorisation shall be granted if the concentration of the active substance or of relevant metabolites in ground water may be expected to exceed the lower value of 0.1 µg/L[4], the maximum concentration laid down by the Commission when including the active substance on Annex I or one tenth of the ADI, "unless it is scientifically demonstrated that under relevant field conditions the lower concentration is not exceeded."

Annex VI is the document that sets out the regulatory decision-making criteria. The statements quoted above indicate that actual measured values under field conditions relevant for the area of use would over-ride estimates and predictions based on the level of

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[3] See FOCUS (1995, 2000) for discussion of the status of validation.

understanding of the basic processes, i.e. the degradation and sorption data required for the active substance and relevant metabolites in the Annex II data requirements for Environmental fate (Directive 95/36/EC).

Directive 95/36/EC itself states clearly the trigger values for higher tier soil degradation studies for active substances (DT50 >60 days in laboratory studies triggers field dissipation studies and DegT90 >1yr in field dissipation studies triggers accumulation studies) and less clearly, the trigger values for higher tier soil degradation studies for metabolites. A laboratory degradation rate study is required for every metabolite that exceeds 10 % in degradation studies on the active substance. However, it is a matter of interpretation whether exceeding the DT50 value of 60 days for a metabolite triggers the further studies that it does for the active substance.

Regarding soil mobility aspects, Directive 95/36/EC sets requirements for sorption studies for the active substance and any metabolites exceeding 10 % in the soil degradation studies. There is also a conditional requirement for an aged leaching study, to address the possibility of highly mobile metabolites present at <10 % which could nonetheless cause a leaching concern. However, this document provides no <u>trigger</u> for undertaking higher tier leaching studies (lysimeter or field leaching experiments) and merely states that "expert judgement" should be used in deciding whether to undertake a study. Similarly the exposure assessments mandated in the Annex III document in Directives 95/36/EC require that suitable estimations of PECgw for active substances and relevant metabolites[5] must be submitted but that "expert judgement is required to decide if additional field tests could provide useful information."

This is the extent of binding requirements for consideration of ground water assessments for active substances and metabolites.

3.2.1.2   EU guidance documents

In recent years the consideration of metabolites (also encompassing degradation, transformation and breakdown products) within Directive 91/414/EEC has provoked much discussion and concern. In response to this, a specific guidance document (Sanco/221/2000 – rev. 10) has been prepared to consider the relevance of metabolites in ground water. This

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[4] For practical purposes FOCUS (2000) have used an operating definition of annual average concentration at 1 m depth until it is possible to predict behaviour in ground water. Note that this definition does not have a legal basis.
[5] Following publication of Sanco/221/2000 rev. 10, this should considered to be "potentially relevant metabolite"

document is largely concerned with the definition of "relevant" since the 0.1 µg/L trigger for ground water does not apply to "non-relevant" metabolites and "metabolites of no concern" (however the document also provides further triggers that require additional data for non-relevant metabolites which exceed concentrations of 0.75 µg/L and 10 µg/L). These aspects of the guidance document are not directly relevant to a general framework for leaching assessment and so are not summarised further in this document. Of more significance is that the guidance document recommends a formal extension of the need to consider the relevance (in ground water leaching terms) of metabolites that reach >5% at two successive sampling times / intervals during degradation studies on the active substance as well as those for which "the maximum of formation is not yet reached" at the end of the study. Less controversially, the guidance document also recommends that all metabolites exceeding 0.1 µg/L annual average in the leachate in lysimeter studies should also be subject to further assessment.

The document further discusses the availability of data from experimental sources (lysimeters and monitoring data) and this can be considered representative of current thinking in the EU. Two particular statements are of relevance although there is no clear attempt to define a hierarchy of other information in relation to modelling studies:

> "For metabolites found in the leachate of lysimeter studies with annual average concentrations above 0.1 µg/L an attempt should be made to assess their leaching behaviour in other European regions with different soil and climatic conditions with the goal to extrapolate the experimental findings to other representative regions of European agriculture."

and

> "Monitoring data from regions with well-documented use of the active substance in question may provide a useful additional tool to supplement model calculations and lysimeter experiments to improve the accuracy and validity of estimates of potential groundwater contamination."

An early draft guidance document on calculation of PEC, including PECgw (7193/VI/99 rev 0.) has now been superseded by other guidance from FOCUS. Therefore further consideration of this document is not necessary.

3.2.1.3   FOCUS guidance documents

As far back as 1995, FOCUS (1995) made some attempt to address a tiered approach to regulatory assessments of ground water leaching potential. However, at that time consideration of the placement of higher tier field data in the scheme was considered to be beyond the remit of the group. A later FOCUS work group (2000) provided information on a tiered approach to the use of available data, within the modelling context. Guidance was also given on the derivation of input values for modelling when faced with a number of experimental values, as generated in a standard environmental fate data package under Directive 91/414/EEC (FOCUS, 2000, 2002).

The same work group (FOCUS, 2000, 2002) also provided recommendations for the interpretations of the results from the relevant ground water scenarios.

"If a substance exceeds 0.1 µg/l for all relevant scenarios, then Annex 1 inclusion would not be possible unless convincing higher tier data (e.g. studies, monitoring or more refined modelling) was available to over-ride the modelling results.

If a substance is less than 0.1 µg/l for all relevant scenarios, then the choice of a realistic-worst case definition for the scenarios means that there can be confidence that the substance is safe in the great majority of situations in the EU. This does not exclude the possibility of leaching in highly vulnerable local situations within specific Member States, but such situations should not be widespread and can be assessed at the Member State level when considering national authorisations.

If a substance is less than 0.1 µg/l for at least one but not for all relevant scenarios, then in principle the substance can be included on Annex 1 with respect to leaching to groundwater. As the scenarios represent major agricultural areas of the EU, such a result indicates that "safe" uses have been identified, which are significant in terms of agriculture in the EU. The scenarios which gave results less than 0.1 µg/l, along with the results of any higher tier studies which already exist, help to indicate the extent of the "safe" uses which exist for the substance. These higher tier studies could include lysimeter or field leaching studies, monitoring and more refined modelling. The results of the entire leaching assessment at the EU level could then be used to assist local assessments of leaching at the Member State level."

3.2.2 Review of existing national approaches for leaching assessments

According to the FOCUS ground water guidance document of 2000 (SANCO/321/2000 rev.2), risk assessment of the leaching of pesticides to ground water for the EU, should be made following a tiered approach. The FOCUS guidance restricts itself to exposure assessment on tier 1 for the EU level and there is no precise guidance on a tiered approach for leaching assessments on a national level. Furthermore during the EU-evaluation process a number of different methods of higher tier assessments have been used by notifiers / rapporteur member states, which indicates that there is a need for consistency. In the review reports, the conclusive product of the evaluation of an active substance and the basic document for the decision, there may be included certain conditions to be taken into account by member states at time of authorisation of products after post Annex 1 inclusion of an active ingredient. For several active substances the following condition is included: *Leaching to groundwater: Particular attention should be given to the potential of groundwater contamination, when the active substance is applied in regions with vulnerable soils/ or climate conditions and risk mitigation measures should be applied where appropriate.* This implies that member states should implement a strategy to handle this condition specified above.

The remit of the FOCUS ground water work group established in 2003 includes providing guidance on higher tier leaching assessment and on harmonisation of risk assessment procedures at national level. Therefore, the Work Group felt that it was vital to get information from the member states on to what extent and how the FOCUS guideline of the first tier assessment is currently used within member states of the European Union and how the countries solve the ground water risk assessment on a member state level. As a first step a questionnaire was put together with the objective of obtaining this information. The questionnaire was sent out by the Commission to the 25 member states (including the 10 new member states). The full questionnaire is included as Appendix 1. Eighteen out of 25 member states provided responses to the questionnaire.

3.2.2.1 The structure of and type of questions in the questionnaire

The main idea with the questions has been to get an answer how member states assess risk for ground water contamination from the use of plant protection products. The questionnaire is divided into four main chapters and eight sub-chapters with totally 28 questions with 15 sub-questions. The aim of the work group has been to limit the number of generic questions and, including the sub-questions, a total of about 27 questions were Yes/No questions or where choices could be made from alternatives.

3.2.2.2   Summary of questions and answers divided into the main topics.

In some cases, mainly non-generic questions, member states provide very similar answers. In other cases, such as generic questions, the answers are more diverse. As a result, the responses have had to be presented in a simplified manner. More details are presented in Appendix 2, which provides a synopsis of the answers by sub-topic.

3.2.2.2.1   General questions

Questions: Asking whether member states are assessing risk to ground water, if FOCUS ground water guidance is used on a national level and if the guideline fulfils the needs. There are also questions about what triggers a ground water assessment, and if a tiered approach is used.

Answers: All member states, except for two that are about to implement an assessment scheme, answer that they are assessing risk to ground water on a national level as a routine procedure and use the FOCUS ground water guidance document. Eight countries say that the FOCUS guidance is fully satisfactory, while the remaining nine have different reasons why the guidance is not fully satisfying their needs. The main reason to the answer " not sufficient" are reasons such as the scenarios are not representing their national environment and, in some cases that, the scenarios are not sufficiently protective (including responses that specific models are needed for consideration of macropore flow in structured soils). One country stated it has very shallow ground water and another country said that the scenarios do not cover all crops.

One question only directed to "new" member states asked what method they had chosen for their ground water assessment scheme. Some of the new member states stated that one or several FOCUS scenarios are used for modelling as well as studies like lysimeters for higher tier assessment. One member state answered that they used the GUS method (Gustafson, 1989). In response to an additional question to the new member states about training possibilities, all of the countries had had some kind of training, but all wished to have more training.

On the sub-question about the experience of technical scientific problems, five countries recommended improvements, e.g. implementations of help/explanations in the models. One specific example was a need for guidance in PELMO in how to treat the relationship between degradation rates of parent, metabolites, and CO_2. More scenarios with macro-pore flow were requested and one country wanted more crops to be added. One country replied that the FOCUS pedological and climatic conditions do not apply in their country.

Thirteen countries answered that the main trigger for a specific national assessment was when the review report recommended that ground water risk should be assessed on a member state level. However, three of these countries also said that other triggers are used on a case by case basis. Four countries have their own triggers. Examples of other triggers are the outcome from lysimeter and other field studies, indications of leachability (i.e. >0.1µg/L) in FOCUS scenarios from the assessment on the EU-level, positive findings from monitoring, experience from earlier national assessments, and divergence of the GAP from the intended use on which the inclusion on Annex I is based.

Fourteen member states used a tiered assessment approach, while one does not currently use a tiered approach and one is planning to use a tiered approach. The responses have been simplified in this paragraph, but details are available in Appendix 2. Some countries with a well defined tiered approach have identified one or more FOCUS scenarios that are relevant for their country and perform further assessment when the prediction concentration exceeds 0.1 µg/L in any of these scenarios. One country uses adsorption and half-life values to trigger to simulations on a national level. Several countries include lysimeters in their tiered approach. One country with areas where the water table is near the ground surface also includes the behaviour in the saturated zone.

Conclusion: Each country has its own specific methods for higher tier assessment, but often countries use similar approaches.

3.2.2.2.2 Regulatory questions

Questions: This topic asks for information on the ground water risk assessment endpoint used by the member states (including whether a safety factor is used), whether information other than simulation results are taken into account in making the assessment, whether there are alternatives to full approval, and whether risk mitigation measures are considered at national approval.

Answers: While the responses are consistent with regard to the limit value of 0.1 µg/L there is some variation considering the procedural definition of the endpoint (e.g. depth, percentile). Since different member states gave different sets of endpoints, there appears to be considerable differences between countries on this topic. However, no country applies a safety factor on the endpoint in national level assessments.

Two countries take decisions on simulations only, while the remaining countries said that they do but added further comments. Some countries pointed out that field experiments (e.g. lysimeters) are used or required before decision is made. Two countries said that their decision is made only on model simulations when no field or lysimeters are available. One of these countries also takes decision based on simulations if the modelling results are below 0.1 µg/L. Another country may use model results only for new active substances. Two countries have field and lysimeter studies as a requirement within their tiered assessment scheme. This may be the case for other countries having a tiered assessment approach in the group of countries replying that they did not make decisions only on model simulations. In conclusion all countries but two do not make decisions only on model simulations when results from higher tier studies such as lysimeters are available.

Member states responded with a number of different approaches to the question regarding different alternatives to full approval that they apply at time of the decision. See Appendix 2 for the details, but the most frequent options chosen as an alternative to full approval were to apply special conditional registration (14 member states), followed by regional or local approval, and special conditions (in both cases seven member states mentioned this as an option), and finally three member states answered that special approval for farmers was an alternative and one additional member state answered that this option is planned but not yet implemented. Only one member state does not have a possibility for alternative approval. See Appendix 2 for details.

Thirteen member states consider risk mitigation measures at approval on a national level. The most frequent measures are related to changes in the GAP, i.e. dose and number of applications, but also restricting use to only non-vulnerable areas.

Conclusions: As reflected in the answers provided by the different member states, differences in the interpretation of the regulatory endpoint between member states are common.

3.2.2.2.3 Specific questions on scenarios

Questions: Do member states use any of the nine FOCUS scenarios as national scenarios or have they defined their own? If a member state uses scenarios of their own, there are additional questions to provide more details.

Answers: Regarding the use of FOCUS scenarios to assess risk for ground water contamination, there is a range in number of scenarios used in different countries from one to

six scenarios. The most frequently used scenarios are Hamburg (five member states); Kremsmünster (four member states); Jokioinen and Piacenza (three member states); Okehampton, Thiva, and Châteaudun (two member states); and Sevilla and Porto (one member state). Four countries said that they have scenarios of their own. One member stated that they use an already validated scenario based on realistic lysimeter studies, and that the scenario is similar to the FOCUS Hamburg scenario. In two other countries, one has two national scenarios and the other country three, all defined as representing realistic worst case scenarios. In one of these countries the colder climate was a reason for developing their own scenarios. The fourth country said they use scenarios that are more realistic compared to the FOCUS scenarios. Two new member states are planning to develop a national scenario. Yet another country, which uses the FOCUS scenarios, considers and evaluates scenarios where national soil and weather data are used.

The three countries not using FOCUS scenarios were asked to provide information on their national scenarios. One country uses a normal and wet regime together with realistic worst case soil and crops according to GAP. Although described somewhat differently the other two countries use weather representative for agricultural areas together with one worst case soil and one realistic soil, both soils being representative for agricultural areas. In one of these two countries, the combination of weather, soil and crops are representing major agriculture areas.

Four countries, different from the three countries having national scenarios, have answered the question about whether weather, soil, or crop properties are most important in defining scenarios. One member state said that rainfall and crops are most important, while another member state said that they consider a fluctuating ground water to be important.

The countries having national scenarios were asked whether they consider their scenarios more conservative (vulnerable) than the FOCUS scenarios. One member state considers their scenario similar to Hamburg but less conservative than Piacenza. Another country has one scenario similar to Hamburg. The third country answered that macro-pore structure and the colder climate are considered in their scenarios. For the rest of the countries this question was not applicable, but one of them considered their scenarios to be equal to the EU scenarios. Four of the countries having national scenarios different from the FOCUS scenarios, consider their scenarios to be of a higher tier compared to the FOCUS scenarios. The country having two national scenarios requires passes in both of them to grant authorisation. The country with three scenarios uses a tiered approach in case leaching is observed in one of the scenarios and finally an expert judgement is applied.

Conclusion: Different regulatory schemes in different countries are quite common. The development of national scenarios may sometimes reflect political/historical background as well as pedo-climatic differences.

3.2.2.2.4 Model used

Question: The member states were asked which simulation model was used in their country.

Answers: The thirteen responses are somewhat confusing, but a simplified outcome based on responses from eleven countries is that two countries use MACRO for the simulation of leaching through macro-pore structure. One of these countries also accepts PELMO/Hamburg as a model/scenario. Three countries use PELMO and of these one also accepts PRZM as both PELMO and PRZM can simulate snow melting. Four countries use PEARL, one coupled with GeoPearl.

Conclusions: Different model recommendations are based on historical preferences and on country specific conditions.

3.2.2.2.5 Parameterisation

Questions: The member states were asked how parameters such as degradation and sorption were selected for use in model simulations. The questionnaire (Appendix 1) included a long introduction providing the main recommendations on parameterisation from the FOCUS Groundwater Scenarios Work Group. The main recommendations are that mean values should be used and that either laboratory or field data may be used. Note that at the time this guidance was developed, methodology for normalisation of degradation was only applicable to laboratory data. The question was divided into first tier and higher tier approaches.

Answers: In initial tier assessments, ten countries use laboratory data for degradation rates while eight choose input data on a case by case basis. All of these countries normalise data according to the FOCUS guidance. However, differences exist in calculating these values since a majority of countries use the arithmetic mean of the available values, six use the geometric means, three have different options based on the specific case, and one country uses 80th percentile DegT50 input value. The dependency of degradation on pH is considered by most countries, but in different ways (see Appendix 2). Three countries consider pH dependency in higher tier assessments.

In higher tier assessments, 12 countries use degradation rates from field data. In four of these countries, the use of laboratory data is also an alternative. Three countries require that field studies should be relevant for their respective countries. All 12 countries normalise degradation data and treat data in the same way as in Tier 1. Eight countries consider degradation data from specific soils to be of higher relevancy, whereas degradation data derived from specific study types such as lysimeters or micro-lysimeters are not necessarily considered more relevant.

In the first tier, all countries use K_{oc} as input parameter for adsorption. Also two countries additionally accept time dependent adsorption, and another country additionally accepts data from column leaching. Fifteen countries use the arithmetic mean for calculating K_{oc}; some use the median if a large number of data are available. One country uses the 80th percentile worst case values. Two countries consider specific dependency on soil properties (e.g. from soil pH).

In higher tier assessments, 13 countries use K_{oc} and the answers of the remaining K_{oc} questions are similar to Tier 1. On the question whether site-specific sorption experiments are accepted as input data, five countries say they use such data, four do not.

Few countries answered the question on use of data from soil-specific degradation and sorption experiments. Since this question is related to an earlier question, this means that a few countries use local input data if available while one country considers the effect of pH in higher tier assessments. Another country uses laboratory data at the first tier and then uses field data at the next tier.

The responses to the questions in this topic indicate that lysimeter and field study results are seen as more important in higher tier assessments than changing the adsorption/degradation input parameters in modelling simulations.

All countries apply quality criteria to experimental data. Some countries have pointed out that studies not fulfilling the quality criteria are not considered in the assessment.

Conclusions:
- Parameter selection in the various countries are quite harmonised (very few exceptions), based on previous FOCUS recommendations.

- The responses to the questions in this topic indicate that lysimeter and field study results are seen as more important in higher tier assessments than changing the adsorption/degradation input parameters in modelling simulations.
- All countries apply quality criteria to experimental data.

3.2.2.2.6 Additional experimental data

For national assessments several member states require additional experimental data which are not available in the EU dossier. Some of them pointed out that this is done on a case by case basis or it is left to the applicant to show that safe use with regard to ground water protection exists also under the relevant national conditions. Most of the member states asking for additional experimental data require or accept lysimeter or field leaching studies. The requirement may be triggered by modelling results exceeding 0.1 µg/L or differing national conditions (e.g. climate), compared to those where studies, submitted with the EU dossier, were performed. In addition, monitoring studies are taken into account by member states for national assessments but only few examples were provided for other specific data (experimental data for refined model input, modelling based on GIS-data), which can be included in the assessment. Six member states indicated that no additional experimental data is required.

Only two member states confirmed they had a national guideline for lysimeter or field leaching studies.

The responses to the questions on the results of the experimental studies indicate that there was probably some confusion about the information collected during a study as well as the explicit endpoint used in the risk assessment. Most member states answering the questionnaire use the annual average concentrations as the endpoints but there are also member states using the highest concentrations.

Nine member states have the option to require post registration monitoring studies under specific circumstances.

Conclusions:
- There is a lack of appropriate national guidelines for the performance of higher tier studies for national assessments.
- The risk assessment endpoints determined from field studies (such as lysimeters) varies among the member states.

3.2.2.2.7 Interrelationship between models and higher tier experiments

Experimental and modelling studies are both considered for the leaching risk assessment at the member state level. Most of the member states answering the questionnaire regard results from appropriate higher tier experiments as superior to model calculations. Only one member state stated that model results overrode results from field studies. All countries, except one, make a joint decision from the results of experimental data and model simulations. The extrapolation of existing experimental data by modelling to national or regional conditions is currently applied only in a minority of member states.

3.2.2.2.8 Handling of metabolites

Most of the member states answering the questionnaire are dealing with metabolites on the basis of the EU Guidance document on the assessment of the relevance of metabolites in groundwater (Sanco/221/2000 rev. 10). One of the member states said that in principle the approach of the guidance document is followed but a few deviations and more detailed criteria have been developed. Two member states (deviating from the guidance document) apply the same criteria for both relevant and non-relevant metabolites. In other words, all metabolites are regarded as relevant (except inherently non-problematic compounds such as carbon dioxide or glucose). Several member states said that discussions on this issue are ongoing. In accordance with the guidance, all member states treat relevant metabolites in the same way as active substances; i.e. the limit value of 0.1 µg/L applies. For metabolites not identified as relevant the situation is partly still unclear: Five member states said they apply limit values as suggested by the guidance document. Eight member states said that they do not have a trigger value for non-relevant metabolites differing from that for the active substance, but only two of them do not distinguish between relevant and non-relevant metabolites according to the answer on the question before.

Conclusion: Members states handle metabolites in ground water differently, based on their acceptance and interpretation of the Guidance Document on the assessment of the relevance of metabolites in groundwater.

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4 GENERIC ASSESSMENT SCHEME FOR PEC IN GROUND WATER (GENERAL OVERVIEW)

At the current time a range of data and approaches are used to determine the PEC in ground water[6] according to Directive 91/414/EEC. FOCUS (2000) has previously provided scenarios and guidance for predicting PECgw at the EU level using simulation models. For practical purposes, this group decided to use an evaluation depth of 1 m, unless simulation models are considered capable of accurately modelling the subsoil processes down to the true ground water level and appropriate data exist. In addition, direct experimental evidence (e.g. field leaching studies, lysimeter studies) can be provided by applicants (see Directive 95/36/EC) and on occasion, these results have been put into further context by the use of further modelling (e.g. inverse modelling, extrapolation etc). Also provision is made in Directive 95/36/EC for the submission of available monitoring data. All of these approaches may be also used by individual member states in their product authorisation, according to national approaches.

At the EU level at least, there is no guidance regarding the relative importance of these different approaches in decision-making. At the national level various approaches currently exist (see review of national approaches in Section 3.2.2), but a more standard generic approach to the process (i.e. relative importance of modelling data, field experiments, monitoring data etc) would be helpful. The aim of this document therefore, is to develop a generic assessment scheme that can be used at both the EU and national level in order to provide a clearer decision-making scheme for pesticide registration.

4.1 Assessment of the representativity, scope and limitations and usability of different study types

4.1.1 Relevance of experimental and modelling studies

The <u>relevance</u> of an experiment or a modelling study to make a contribution to the assessment of ground water vulnerability for the specific protection goal is the <u>key factor for balancing</u> and defining the interactions of experimental and modelling studies.

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[6] "Ground water" is not defined within Directive 91/414/EEC. However the working definition used by FOCUS is all water that is at least 1 m below the surface of the ground and in the saturated zone. This means that no water less than 1m depth is considered as ground water. This also means that below 1 m, the soil has to be saturated before the pore water is considered as ground water.

Before an experiment or a modelling study can be used for the assessment of a pesticide for Annex I inclusion or national registrations with regard to possible exposure of ground water, its relevance needs to be checked.

The relevance of each individual study depends on:
    a) the reliability (i.e. the study is performed using state-of-the-art and robust methodologies and documented adequately so results can be trusted) and
    b) the usefulness, (i.e. the results or conclusions of the study deliver a contribution to the risk assessment in question).

With regard to usefulness, the term "relevance" covers two aspects:
    (i) the experimental or modelling study itself is appropriate for the use conditions considered for Annex I inclusion or national registration
    (ii) the experiment or modelling study is useful for an extrapolation to different use conditions or environmental scenarios.

This implies that studies performed outside the EU can be used in the EU procedures if the relevance of the study has been proven. The same criteria apply consequently also on the national level.

4.1.2   Study types for leaching assessment

A wide range of factors determines the fate of pesticides in the environment. These include chemical characteristics (vapour pressure, solubility, adsorptive behaviour, chemical structure, and degradability), environmental characteristics (precipitation, temperature, wind and soil, sediment and water characteristics), and agricultural practices (cropping practices, application methods, timing of application, and landscape).

Leaching of a pesticide depends on both its persistence and its mobility, as well as on the soil physical transport properties and transport processes. With regard to the substance properties, persistence is a measure of the resistance of a pesticide to being chemically transformed, most commonly described by the DegT50, while mobility is commonly described by the soil-water partition coefficient, the K_d. Both are usually measured in laboratory studies. Environmental factors as well as chemical and biological processes affecting persistence and mobility of the pesticide fate vary in space and in time. Consequently, when facing such complexity it is often difficult to assess fate accurately for the purposes of risk assessment based solely upon these data. As a consequence

considering other methodologies is necessary to gain an understanding of fate, behaviour, and exposure and their implications within a context of risk.

To provide guidance the FOCUS group has compiled a list of different study types (including detailed description) useful for leaching assessment or for generating parameters for modelling and a list of which information (data) that can be gathered from which study type. This review of current information and experiences available within the European Union, the USA and other countries (SETAC, OECD, FOCUS, PSD, EPA, FIFRA) is presented in Appendix 3.

4.2 General principles of a generic assessment scheme for PEC in ground water on EU and national level

The general concepts that have been followed in developing a tiered assessment scheme for prediction of concentrations in ground water are:

a) simplicity (i.e. can be clearly understood)

b) foundation on scientific criteria (to be uniformly applicable)

c) consistency

(i.e. to avoid logical inconsistencies between EU level and National level or between different Member States at the National Level).

The same regulatory principles and scientific assessment criteria should be applied at the EU level and throughout the National authorities (uniform principles), to ensure that differences in registrations on a national level are based on differences of environmental conditions, management practices, and mitigation options. In other words, the criteria used for the initial choice of pesticide properties (i.e. Tier 1 in the scheme below) should not vary in different schemes.

These concepts are applicable to schemes for assessing ground water contamination potential at the EU or Member State level <u>even though</u> the different levels have <u>different objectives</u> for pesticide registration (see Section 3.1).

The broad intention of any tiered scheme is that the initial (or earlier) tiers are quick, simple and cheap to undertake and allow the items that clearly do not cause any concern to be passed. The later (or higher) tiers are more complex and expensive but should provide a more realistic (less conservative) result. This philosophy is shown in Figure 4-1.

Realism/Effort

Early Tier

Less
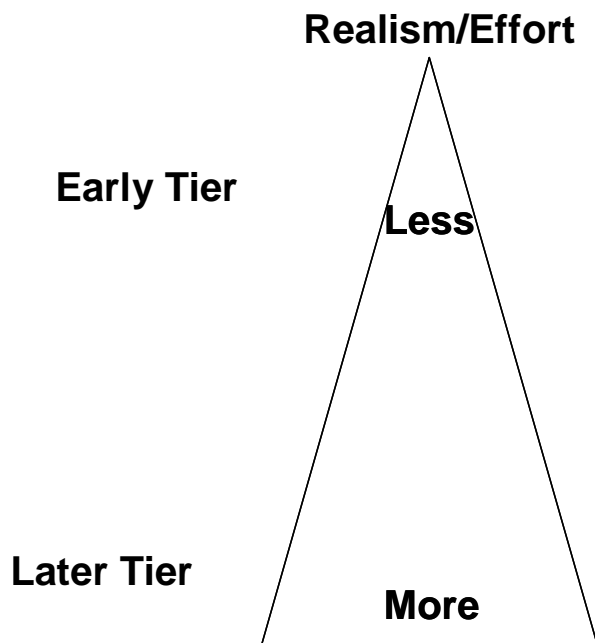
Later Tier

More

Figure 4-1. Schematic representation of tiered approach to issue resolution

With respect to ground water leaching schemes, the group's aim is to have an earliest tier (tier 1) that is always more conservative (i.e. overestimates actual exposure), while the later tiers are more realistic (i.e. closer to actual exposure). Therefore, by definition the later tiers should give lower estimates of exposure while concurrently being more realistic. This is ensured by the choice of validated models (default assumptions) and choice of parameters (laboratory) and conservative nature of the scenarios in earlier tiers (see work of APECOP, Vanclooster et al., 2003). Validation of the tiered approach is provided by Hardy et al. (2008) with conditions similar to the FOCUS Hamburg scenario.

However, in reality this may not always occur given the fact that the existing EU FOCUS scenarios are only aimed to be representative of an overall 90th percentile, and that whether this is even achieved cannot be rigorously proven. Also some of the assumptions inherent in the existing FOCUS EU or individual Member State scenarios may not hold true for all compounds at all times (for instance the default changes to rate of degradation with depth) and could, in theory, lead to underestimates of the extent of leaching on isolated occasions.

Nonetheless in the overwhelming majority of cases, the existing FOCUS ground water scenarios should provide a conservative first step for EU assessments. The work group further considers that this approach is appropriate in the present context. Consideration of

national scenarios for simulation modelling is not within the group's remit, but in general the individual member states consider them to be an acceptable initial tier (according to the questionnaire all member states use a tiered approach and those with a national scenario for simulation modelling appear to be prepared to make favourable regulatory judgements on the basis of the model output only, when predicted concentrations are <0.1 µg/L).

4.3   Proposal for a generic tiered approach

Following consideration of the types of data that are available for determining the PECgw, the risk assessment approaches have been categorized into four tiers based on the availability of information.

- All PECgw modelling assessments based on data according to the requirements in 91/414/EEC in combination with standard FOCUS (2000) scenarios or the standard national ground water scenarios[7], are classified as Tier 1.
- Higher tier (more refined) modelling approaches are classified as Tier 2, and supersede assessments at Tier 1[8]. These approaches can be categorized as:
    - (a) parameter refinements for modelling (e.g. non-equilibrium sorption measurements)
    - (b) scenario refinements (e.g. GIS data, hydrogeological data; characterisation of vulnerable situations or 'risk areas' to enable more targeted simulations for specific crops)
- Combinations of the modelling and refined parameters from Tier 2, as well as experimental approaches set into context by modelling, or advanced spatial modelling and in the future potentially, other modelling approaches are classified as Tier 3, and supersede assessments at Tier 1 and 2.
- Monitoring of ground water (with appropriate reality checking) is seen as the highest tier (Tier 4) and supersedes assessments on Tier 1, Tier 2, and Tier 3.

Where there are a number of options for a given tier, undertaking all options is not necessary. Any single option is sufficient. However, any approaches should be justified using all appropriate data available.

This assessment scheme is outlined in Figure 4-2 and subsequently discussed in greater detail.

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[7] At this time many member states do not have national ground water scenarios. Nonetheless, if available/developed these approaches could easily be incorporated at Tier 1.

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┌────────┐                    ┌──────────────────────────────────────┐
│ Tier 1 │                    │                  1)                  │
└────────┘                    │ Standard scenarios with lab or field │
                              │           degradation data           │
                              └──────────────────────────────────────┘
                                    │                      │
                                    ▼                      ▼
┌────────┐        ┌──────────────────┐        ┌──────────────────┐
│ Tier 2 │        │        2a)       │        │        2b)       │
└────────┘        │   Modelling with │        │   Modelling with │
                  │ refined parameters│        │  refined scenarios│
                  └──────────────────┘        └──────────────────┘

┌────────┐  ┌────────────┐ ┌────────────┐ ┌────────────┐ ┌────────────┐
│ Tier 3 │  │    3a)     │ │    3b)     │ │    3c)     │ │    3d)     │
└────────┘  │  Combined  │ │  Advanced  │ │Higher tier │ │   Other    │
            │ modelling  │ │  spatial   │ │  leaching  │ │ modelling  │
            │  refined   │ │ modelling  │ │experiments │ │ approaches │
            │ parameters │ │            │ │set into    │ │            │
            │ & scenarios│ │            │ │context by  │ │            │
            │            │ │            │ │ modelling  │ │            │
            └────────────┘ └────────────┘ └────────────┘ └────────────┘

┌────────┐                    ┌──────────────────────┐
│ Tier 4 │                    │          4)          │
└────────┘                    │ Ground water monitoring│
  * Mitigation possible       └──────────────────────┘
    at all tiers
```

Figure 4-2. Proposed generic tiered assessment scheme for ground water.

4.3.1   Tier 1 at EU and National Level

The first tier of the assessment scheme comprises all PECgw modelling assessments based on data according to the requirements in 91/414/EEC in combination with standard (FOCUS, 2000) or national ground water scenarios.

Guidance on the selection of pesticide input parameters for models at the EU level is given by FOCUS (2000, 2002). Further guidance on selection of appropriate degradation kinetics as well as the averaging procedure for the representative modelling endpoint is provided by FOCUS (2006). On the basis of the general principles stated earlier, these same pesticide inputs (i.e. those selected for EU level) should be used for national registrations at Tier 1.

At the EU level FOCUS considers that a predicted annual average concentration of <0.1 µg/L at any single scenario constitutes a safe use that would enable an Annex I listing (see FOCUS, 2000). However, as also noted in Section 9.4 this is not currently accepted by

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[8] Options a and b in Tier 2 are used in combination with FOCUS models or national models.

member states. Pass criteria at the national level are currently set by individual member states.

4.3.2   Tier 2 approaches (Tiers 2a and 2b) at EU and National level

4.3.2.1   Modelling with refined parameters (Tier 2a)

Additional information on the pesticide behaviour in soil can be used to refine the parameters from the Tier 1 modelling step (basic parameter set as required by 91/414/EEC).

This may include better data on particular processes (e.g. sub-surface degradation, non-equilibrium term sorption) or on particular conditions (i.e. degradation rate data on additional soils) relevant to a particular crop or member state.

This additional information could be for instance:

- a higher number of K_{oc}/DegT50 measurements that allow parameter refinement
- non-equilibrium sorption parameters (long term sorption)
- K_{oc}/DegT50 from different depths in the soil profile
- a correlation of K_{oc}/DegT50 to soil properties
- K_{oc}/DegT50 in specific soils for use area
- paired DegT50 / K_{oc} values
- data on plant uptake
- data on volatilisation from soil surfaces
- degradation kinetics other than single first order
- data on soil photolysis

The refined pesticide input values are then to be used (in Tier 2a) with the modelling scenarios from tier 1 (EU-FOCUS or the national scenarios). The results can be used e.g. to define mitigation with regard to the use area based on soil and compound properties (if relationship exists between e.g. K_{oc} and/or DegT50 with specific soil properties). See Section 7.1 for more detailed information.

Pass criteria would be the same as for Tier 1.

4.3.2.2   Modelling using refined scenarios (Tier 2b)

GIS approaches or appropriate statistical data on cropping, soils, climate, etc may demonstrate that existing scenarios (i.e. at Tier 1) are not appropriate or not sufficient for a given crop or in a given member state. The refinement of scenarios with respect to soil,

crops or climate implies the development of scenario(s) that is/are tailored more specifically for the intended use(s) of the pesticide compared to standard FOCUS or national scenarios.[9]

The refinement of scenarios could lead to:
- scenarios tailored more specifically for intended use (compared to FOCUS/national scenarios) with respect to soil, crops, climate
- define mitigation measures with respect to use areas / use conditions

The scenario refinement must be shown to be an improvement with respect to realistic representation of the specific soil, weather, and agronomic conditions, considering the objective of the protection goals. The tools for scenario refinements can also be used to define mitigation measures to ensure that uses of the pesticide do not violate the protection goals.

Examples:
- Considering realistic depths to ground water
- Identifying areas with confined ground water only
- Considering interactions with mitigation [see Chapter 6)]
- Considering specific crops not covered by FOCUS
- Considering specific conditions of use (e.g. greenhouse)
- Identifying characteristic combinations of crops/soil types/ground water conditions

The refined scenarios are then to be used (in Tier 2b) with the modelling parameters from Tier 1. For detailed approaches see Section 7.2 and Appendices 4 and 5.

Pass criteria are in principle the same as for Tier 1. The assumptions that lead to the revised scenarios will define the actual approvals granted.

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[9] In this circumstance the scenarios for the major crops provided by FOCUS (2000) for EU-wide assessment are probably less likely to be open to refinement than those crops not covered (or only peripherally addressed) by FOCUS. Similarly member states with well-defined scenarios for relevant crops are less likely to be open to refinement than those in member states who do not have defined scenarios or whose scenarios do not cover the crop of interest.

4.3.3 Tier 3 leaching assessment

4.3.3.1 Tier 3a: Combination of modelling with refined parameters and refined scenarios

Where relevant to the proposed use pattern, the refinements detailed in Tiers 2a and 2b (see above) can be combined to provide an assessment based on both approaches. This is seen as a further refinement of the assessment and hence supersedes Tier 2. See also Section 8.1.

4.3.3.2 Tier 3b: Advanced spatial modelling

Spatially-distributed leaching models provide the user with maps of the predicted leaching concentrations in the intended use area or in a climatic zone. Frequency distributions and percentiles of the leaching concentration can be directly inferred from these maps. Spatially distributed leaching models can therefore be important tools in higher tier risk assessments.

Spatial patterns of pesticide leaching can be directly simulated with process-based models, for example one of the FOCUS leaching models. Most approaches to spatially-distributed, process based numerical modelling come down to running a leaching model for several (often more than 1000) scenarios and putting the results in a map.

The scenarios are usually constructed by spatially overlaying basic maps in a Geographical Information System. With respect to pesticide leaching, maps of soil-types, climate-classes, crop-types and ground water depth-classes are of particular interest. The disadvantage of process based spatially distributed models is that they contain a large number of parameters, which may be difficult to identify directly or which may not be available at larger scales. Additionally the quality of the underlying data must be carefully considered (the reader should be aware that pictorial representations of the data can sometimes provide false re-assurance regarding the detail of the information on which the assessment is based).

If the sets of soil profile and weather data are available for the entire intended use area (and are considered of sufficient quality), then the regulatory endpoint can be calculated directly with a spatially distributed leaching model.

For building a set of pan-European spatially distributed pesticide leaching scenarios, soil, climate and cropping data bases are needed. The MARS (climate) and Corine (land-use) data bases cover the entire European Union. The Soil Profile Analytical Database of Europe, release I (Jamagne et al., 1995), however, has serious limitations. The most serious limitation is that only 75% of the agricultural area of the EU-15 could be assigned a soil

profile (Tiktak et al., 2004). Also, in many cases, the assigned soil profile is not an agricultural profile. This implies that it is not yet possible to build a process based, spatially distributed leaching model, which covers the entire EU. This also implies that it is not yet possible to calculate the regulatory endpoint directly from a spatially distributed pesticide leaching model.

At the national level, the situation can be different. Some countries (e.g. The Netherlands) do have sufficient soil information available to build a full spatially distributed pesticide leaching model and the GEOPEARL model is already in regulatory use for the Netherlands.

Further details on this can be found in Section 8.2 and details of the methodology are presented in Appendix 5.

4.3.3.3 Tier 3c: Higher tier leaching experiments set into context by modelling

Determining the risk of ground water contamination from pesticides involving the use of simulation models is a highly effective method. It enables the quantification of a value that cannot be directly measured without considerable efforts (i.e. the flux weighted annual average concentration at a specified depth) as well as the variation of the results in different scenarios. Therefore the leaching risk of pesticides in a variety of conditions can be rapidly and cost-effectively assessed. Simulation models predict results on the basis of a number of assumptions that are agreed to be generally applicable. However, simulation models are bound within the limitations of conceptual understanding of the processes actually occurring in reality and their mathematical and technical realisation in modelling software.

Experimental data directly measuring the concentrations (instantaneous, averaged over time etc) leached under field or lysimeter conditions constitute a different approach to addressing potential leaching issues. However, as with any data derived under outdoor conditions they may only be directly relevant to the climatic, pedological and agronomic (crop, timing, application rate etc) conditions in which the studies were conducted. GIS approaches and simulation modelling can be used to determine a location and conditions expected to be relevant to the protection goal. This information can then be used to site the experimental study at the appropriate location and hence significantly increase the likely applicability of the experimental results (so called "pre-processing" of the experimental data). Another option to obtain conditions relevant to the protection goal would be to collect appropriate soil monoliths in a lysimeter station and modify the upper boundary conditions accordingly, e.g. the amount and pattern of rainfall to obtain by additional irrigation. This may mean that various existing aspects of currently accepted guidelines will not automatically be acceptable in the future.

Once the experimental data are available, an assessment of the results should be undertaken to address any issues about uncertainty in a limited experimental data set. Simulation of the experimental study conditions should be undertaken using soil-specific or conservative inputs for DegT50 and K_{oc}. Only when the simulation results predict leaching of >0.1 µg/L (corrected for application rates, see Section 8.3.4 for a more detailed explanation of this "entry criterion") are the experimental data considered as acceptable for further assessment.

Any lysimeter data that pass this assessment are subjected to an inverse modelling process to derive DegT50 and K_{oc} values. These should then be averaged with the other existing experimental data in the regulatory package (but given a greater weighting) to derive final DegT50 and K_{oc} values for input into the standard FOCUS scenarios. The results of these simulations are then the regulatory endpoints. Further detail on all these approaches is provided in Section 8.3.4. Pass criteria would be the same as for Tier 1.

Note that the guidance for inverse modelling approach described in Section 8.3.4 is not applicable to field leaching studies and no specific guidance has been provided at this time for deriving appropriate DegT50 and K_{oc} values from such studies. However the work group believes that such approaches can be undertaken in the future based on reasonable scientific principles by analogy to the process described for lysimeter studies.

4.3.3.4   Tier 3d: Other modelling approaches

At this time the view of the FOCUS work group is that other modelling approaches (for example 3-D modelling) are not sufficiently developed for regulatory use at a high tier of the risk assessment scheme. However the work group expects that the science of this will develop in the future and hence considers that current research applications may, in time be usable for regulatory purposes.

Further information on existing modelling approaches that have the potential for regulatory use in the higher tier of the ground water risk assessment scheme is provided in Section 8.4.

4.3.4   Tier 4 (Monitoring)

Ground water monitoring data are seen as the highest tier of assessment since the actual concentrations in ground water are directly measured rather than being estimated by modelling approaches or approximated from small scale field studies.

For existing pesticides monitoring data can be useful at both the EU level and the national level. For instance, representative data from one member state could demonstrate a "safe use" for the EU evaluation. For new active substances historical monitoring data are clearly not available, but post-registration monitoring programs may be possible.

Monitoring data can include the results of dedicated analyses of ground water by notifiers or other agencies (i.e. water companies, environment agencies etc) where there may be a detailed initial assessment of the relevance of the monitoring points (for example, by knowledge of historical compound usage in the area and characteristics of the aquifer) and certain minimum quality criteria are demonstrated.

A detailed discussion of approaches to monitoring studies and guidance on conduct of studies etc is provided in Chapter 9.

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5 INTERACTIONS BETWEEN ASSESSMENT SCHEMES ON EU AND ON NATIONAL LEVEL

5.1 General interactions between the assessment schemes

The interactions between the assessment schemes on EU and on national level are illustrated in Figure 5-1.

The starting point will always be the EU level in which the general risk characterisation will be undertaken. This assessment will show, in general terms, how great the possibility of the PECgw exceeding 0.1 µg/L is likely to be and whether higher tier risk assessment is necessary to refine the initial simulations obtained at Tier 1. These results need to be considered when assessing the actual product authorisation at the National Level.

Generally national assessments likely will <u>start</u> from the level at which safe use is demonstrated at the EU level, although there may not be a strict relationship between the two[10]. If a Tier 2 assessment is needed at the EU level, the product at the same GAP on the same crop is unlikely to pass at Tier 1 on the national level, if the conditions in the member state are comparable to the relevant scenarios at EU level. In such a situation, starting the national assessment immediately at the Tier 2 level may prevent the need to spend time and effort demonstrating the expected failure at Tier 1.

Higher tier data provided for the EU assessment level are not necessarily specifically applicable to the particular national level. For instance, a lysimeter or field leaching study undertaken in a northern European country to demonstrate safe uses at the EU level (Tier 2.1c) may not be considered relevant for a southern European country without an additional assessment of the relevance of the study for southern Europe. In this case, other Tier 2 data may be required to demonstrate safety in the particular national conditions. Therefore, progressing to a higher tier for the national scheme than was necessary for the EU assessment could still be necessary.

Mitigation will play a role at all decision tiers at the EU and at the national level to identify if approval can be given according to the respective protection goals.

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[10] Only if the national authorisation is for a product which has an inherently much lower risk than the representative use assessed at the EU level on the basis of FOCUS scenarios, would it be sensible to start the national assessment from a lower tier than the EU assessment.
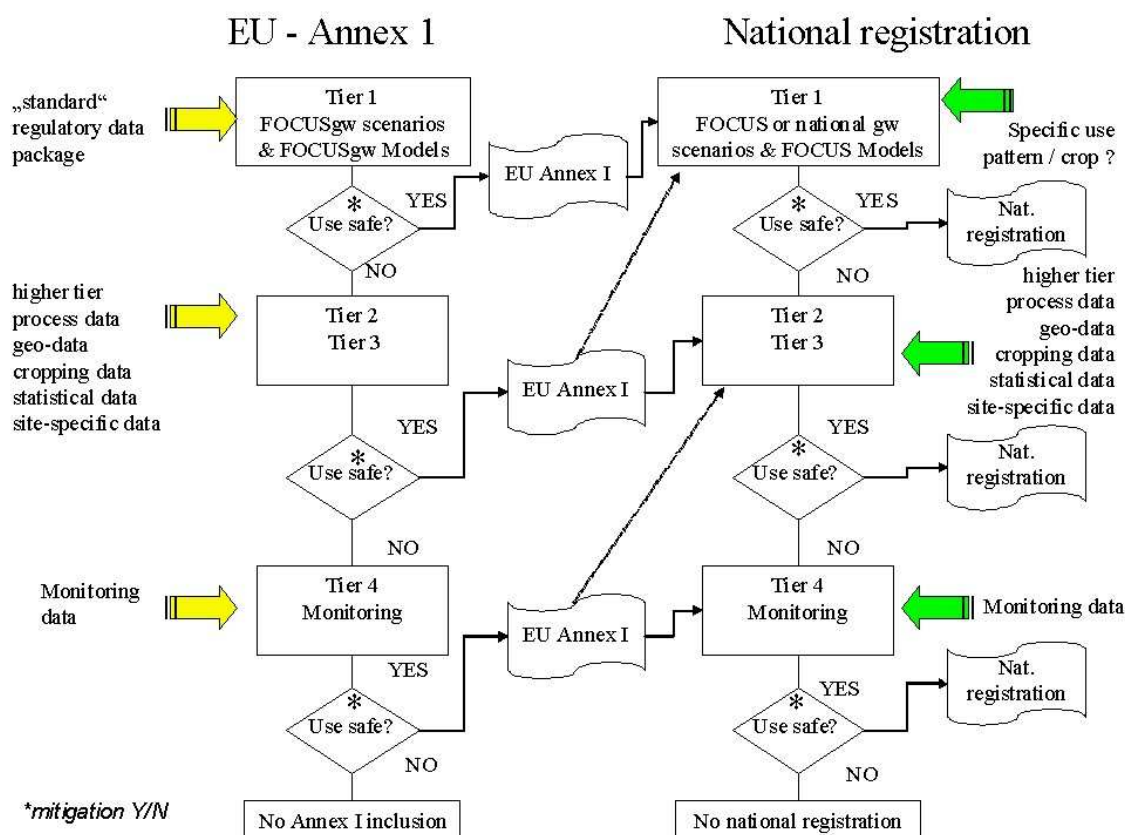
Figure 5-1. Illustration of likely interactions between EU and national assessment schemes.

5.2   Preferential flow in EU and national assessment schemes

In considering the interactions between EU and national assessment schemes, the issue of the regulatory significance of preferential flow should be specifically addressed. Preferential flow is a general term that covers all types of non-chromatographic flow, including defined mechanisms such as macropore flow and finger flow. There is scientific consensus that these processes occur under field conditions. However, cracking heavy clay soils are usually not a ground water problem, since the subsoils usually contain a sufficiently think impermeable layer. They are therefore discharge areas in the landscape, not recharge areas, and there is no (abstractable) ground water useable as a drinking water supply underlying these kinds of soils. Instead, macropore flow in these soils must be considered as a surface water problem, where subsurface drainage systems discharge excess water into ditches and streams. This consensus view has been recognized by FOCUS already, as several of the FOCUS surface water scenarios represent this kind of hydrogeological setting.

Although macropores do exist in highly permeable sandy soils, they do not dominate the hydrology to the same extent, and can therefore probably be safely ignored in ground water

64

leaching calculations. Finger flow can affect movement in sand soils, but there are no models that use commonly available parameters. In less permeable sandy loams and loams, preferential flow can significantly impact pesticide leaching in soil, and in these cases the extent to which preferential flow is continuous to greater depths is an important question for an assessment, especially for deeper ground water which is abstracted for drinking water. Fissured moraine materials and fissured chalk and limestone, both overlying ground water reserves, are examples of hydrogeological situations where preferential flow can be important even at great depths. This has been recognized by FOCUS ground water, where MACRO is used to calculate leaching in the Châteaudun scenario (loamy soil overlying fractured limestone).

For risk assessment purposes, experimental studies incorporating the phenomenon of preferential flow are extremely difficult to undertake due to the inherent spatial heterogeneity of the soil. Simulation models are able to incorporate various types of preferential flow to predict the effect of this process on pesticide leaching. The spatial variability of the process still poses a significant challenge to verifying the predicted outputs of the models. However, the effect of preferential flow must be considered where this poses a significant impact on ground water. The best known model to address an aspect of preferential flow is MACRO, which simulates macropore flow through consideration of soil aggregate size. Newer versions of other models, such as PEARL, now also incorporate mathematical routines to address various preferential flow mechanisms.

In the existing EU assessment scheme the FOCUS scenarios employ the MACRO model at one site only (Châteaudun) to provide a comparison of results to those obtained with chromatographic flow models (PRZM, PELMO, PEARL). However, these results are not used directly in decision-making on Annex I listing. At the national level various member states (e.g. Denmark, Sweden, UK) use the simulation results obtained from MACRO in decision-making for product registration.

For harmonisation of the assessment schemes between the EU and the Member States (and between Member States), FOCUS has already noted (see earlier text) that differences in between assessments at the EU and National Level should be based on differences in environmental conditions/management practices rather than on pesticide parameters.

There is no scientific consensus regarding whether some preferential flows (e.g. macropore flow and bypass flow in cracking clay soils) result in movement to ground water and on the spatial significance of all these processes. However, member states who consider that

preferential flow leading to ground water exposure is relevant for their soil types, have a justification (at the national registration level) for taking these processes into account when making their assessments.

6 CONSIDERATION OF RISK MITIGATION AND MANAGEMENT ON EU AND ON NATIONAL LEVEL

As discussed in Chapter 3 the broad endpoints of the tiered approaches are different at different political levels (i.e. EU evaluation, national authorisation). However, this can still be consistent with a common framework for risk assessment at all the geographical levels.

At the EU level, the aim of risk characterisation is to identify safe uses for at least one relevant crop and a significant area within the European Union. In contrast, at the national level authorisation of a specific plant protection product for actual use in the relevant agricultural, soil and climatic conditions is considered. Member states currently have different views, or non-stated policies on what percentage of "safe use" is acceptable when granting an authorisation. They also have different abilities to mitigate or manage a potential risk (e.g. application restrictions to certain timings, soil types, defined areas etc).

Because both EU and national assessments will occur for each pesticide, the interactions between the schemes should be considered. This will maintain consistency and minimise duplication of work.

A working definition for risk mitigation with regards to the protection of ground water is:
> Measures taken to adjust or restrict the use of a pesticide to obtain a favourable risk assessment. These steps can be based either on knowledge of the behaviour of the specific active substance, and/or on knowledge of the variability in the environment, and/or differentiation in the use of application methods.

6.1 Important aspects affecting or used in risk mitigation

6.1.1 The GAP in the EU evaluation of active substances relative to the GAP on a national level

When an active substance is evaluated at the EU level, the aim is to identify at least one use that is acceptable considering both possible effects on human health and the environment. The number of uses evaluated in the EU process is usually limited to one or a few representative crops. Therefore, the assessment of leaching to ground water on the member state level will not usually be based on the same use pattern as the assessment during the EU evaluation process. Therefore assessments carried out on the EU-level will not

necessarily be directly applicable to the authorisation procedures on the member state level. This especially is true for the identification and implementation of risk mitigation measures.

The GAP defines the crops, dose, number of applications, recommended time between applications, and recommended timing/crop stage for uses on each specific crop. This information is used in the modelling simulations and other aspects of the risk assessment. Note that efficacy and application methods are not evaluated at the EU level, but only at the member state level.

6.1.2   Dose related risk mitigation

Under risk mitigation related to the dose, all measures that lead to a lower actual input of the active substance into the soil can be considered. This lowering may be achieved by mixing the assessed active substance with other active substance/s, resulting in the necessity for a complete new risk assessment in all areas including efficacy studies on the relevant crops. This approach is only considered on the member state level. Another way to lower the amount which reaches the soil is to apply the pesticide at a later growth stage with higher interception. Since this may result in lower efficacy, this mitigation measure can also be expected to be more country specific. Since all measures to lower the amount reaching soil must be accompanied by efficacy data, this type of risk mitigation will in practice only be applicable on the member state level. Lowering the number of applications may be possible at both EU and MS level, but very likely also this adjustment has to be based on efficacy trials. In certain cases the application may be restricted to every other year or even longer intervals. If a particular active substance is used only on specific crops this kind of risk mitigation may already be covered by the crop rotation according to good agricultural practice. However, the possibility that the same active ingredient could be applied to other crops in the rotation must be considered, so mitigation should take into account all uses of the active substance in the crop rotation. Therefore crop rotation is a mitigation measure usually only applicable at the member state level.

6.1.3   Using more effective application methods

Changing the method of application is likely to be more important as a risk mitigation measure to reduce the impact on surface water rather than on ground water. A reduction of the risk for ground water will be achieved by reducing the dose of the active substance reaching the soil. Using band sprayers, which are used in crops growing in rows, such as sugar beets, leeks and other vegetables, may reduce the dose significantly. This application method is used in most European countries. Therefore, this could in principle be used as a method for risk reduction both at the EU and member state level. As a prerequisite there is a need to identify a (may be crop-specific) reduction rate from the use of this method. In this

circumstance particular attention has to be given to the definition of the application rate (i.e. amount of active substance per area actually treated vs. amount of active substance per whole field area). There is only a reduction in risk if the amount of active substance in the whole field is reduced.)

6.1.4   Pesticide properties correlated to soil properties

Pesticide properties are here related to both active substances and metabolites. Leaching may be influenced by the effect of soil properties on transformation and adsorption.

For many compounds the most important factor for adsorption onto soil is the content of organic carbon, but other soil properties (e.g. clay content) may also play a significant role. Another important influencing factor may be the pH-dependency of transformation and adsorption. Knowledge of these effects is mainly derived from laboratory studies. According to the requirements of Annex II and the guidance of the FOCUS groundwater scenarios work group, the pH-dependency of the active substance and metabolites has to be checked and considered, if appropriate. If the assessment identifies a pH range which could result in possible leaching of the substance to ground water, the EU recommends to the member states to consider the problem when granting authorisations. This statement is included in the Review Report and in the Directive of inclusion of the active substance. In this case the combined consideration of substance properties and environmental properties (such as soil pH) may result in risk mitigation by excluding the use in certain defined areas, where a risk for leaching is identified. This risk mitigation step can consist of excluding use in either specific geographical areas or soil types. Geographical exclusions allow for the easy identification of restricted areas at time of the authorisation of a product. Soil exclusions require a well developed system of both enforcement and support by competent local authorities and/or advisers. In addition, an appropriate post registration monitoring programme might be required. An extensive geographical data base providing soil properties on the EU and member state level would be helpful to identify and enforce the options for specific cases.

6.1.5   Hydrogeological properties

Leaching may also be enhanced in areas where the hydrogeology is vulnerable to movement to ground water. Using GIS data on the EU level (when the necessary data are available) will give information on geographical areas with environmental properties that may lead to a risk for ground water contamination of a specific compound. As discussed earlier, this assessment can result in identification of vulnerable areas within EU, but also can lead to identification of "safe" areas. If one safe use is identified, an active substance can be registered at the EU level. If there were indications from other FOCUS-scenarios of potential

risk for ground water contamination, this risk would need to be assessed by member states. These vulnerable areas have to be identified on the member state level. As discussed previously for soil restrictions, clearly identified areas where restrictions apply and competent local authorities and advisers are prerequisite for successful risk mitigation.

6.1.6 *Mitigation related to timing*

Depending on the combination of environmental conditions and substance properties, mitigation may also include the timing of applications. Such restrictions should be based on the knowledge of risks identified with a set of environmental conditions such as climate and soil properties, but also include substance properties, e.g. DegT50.

6.2 Examples of risk mitigation measures

The following risk mitigation measures are examples of possible label restrictions included in the authorisation of certain plant protection products in some countries and may serve as an illustration to the various aspects discussed above:

Dose related risk mitigation

- The maximum load of this product containing *active substance* is restricted to *x* g (alternatively *x* litre) per ha and year.
- The maximum application rate for *active substance* of *x* g per hectare and year must not be exceeded.
- This product must not be applied before tillering. (in order to increase interception)
- Products containing the active substance *active substance* are not to be used more than once a year on the same area
- In those areas identified by the designated authority, the product must not be applied more than once a year on the same area.

Pesticide properties in correlation to soil properties

- This product shall not be used on soils with less than *x* % organic matter. (may also be applicable to e.g. percentage of clay soil)
- Not to be used on the following soil types: pure sand, slightly silty sand and slightly clayey sand.
- Not to be used on the following soil types: pure sand, slightly silty sand and slightly clayey sand with an organic carbon content below *x* %.

Hydrogeological properties

- This product is not recommended for use on karstic soils with very small top soil layer (could be a voluntary recommendation)
- Not to be used in catchment areas of ground and spring water supply works, mineral springs and drinking water reservoirs or other sensitive ground water areas."

Mitigation related to timing

- This product must only be applied from 1st February in the year of harvest until the specified latest time of application. (in order to reduce possible ground water contamination from autumn applications.)
- Not to be used between DD.MM and DD.MM.
- Not to be used on drained soils between DD.MM and DD.MM.

6.3 Conclusion

On EU level only general recommendations for risk mitigation measures can be given based on the evaluation of the properties of the active ingredient(s) and the risk assessment made for the representative formulation in relation to the EU scenarios.

Detailed risk mitigation measures with regard to the protection of ground water against contamination with active substances or relevant metabolites require detailed knowledge of local environmental conditions and enforceable mitigation measures. They are therefore mainly allocated to the authorisation procedure on the member state level. In most of the cases risk mitigation measures will be related to restrictions imposed with the authorisation of a certain plant protection product. Like any restriction in relation to the use of pesticides measures aiming at the protection of ground water have to be checked with regard to their practicable use prior to implementation. Applicators must be able to recognise the conditions of allowed or prohibited use and (if appropriate) must have access to any necessary data. On the other hand sound advice as well as enforcement capacities must be available from the competent authorities.

Due to the fact that risk mitigation measures are mainly subject to MS considerations the discussion in the context of this Guidance Document is restricted to the general aspects and specific examples described above.

7   APPROACHES FOR TIER 2 ASSESSMENT

7.1   Pesticide parameter refinement (Tier 2a)

In Tier 2a parameter refinements can be made so that the pesticide-specific input for the pesticide degradation and sorption processes can be incorporated in the assessment. The remaining modelling parameters, i.e. the soil, crop, and climatic parameters, are considered to be part of the scenario and are not modified. Also the basic modelling framework of Tier 1 is maintained, so that pesticide flow and transport in soil is still considered to be a 1-D chromatographic flow process. While changes in other modelling parameters and the basic modelling framework can be made when scientifically appropriate, such modelling work would then be classified as belonging to other tiers. Table 7-1 gives an overview of the relevant processes which result in refinements included in Tier 2a. More details are given in the following sections.

Table 7-1. Overview of the relevant processes resulting in refinements included in Tier 2a.

Section	Process	Parameter in Tier 1 model	Proposed Refinement	Remark
7.1.1	Soil specific sorption and degradation	Degradation rate, K_d, K_f, N	• Include additional degradation rates • Modify sorption and degradation in terms of known soil properties, exploiting clear relationships between soil properties and degradation and sorption	• Additional degradation rates improve the data base for parameter selection • Includes subsoil degradation • Substance specific degradation rates for changes of degradation rates with depth
7.1.2	Photolytic degradation	Degradation rate	Include a thin soil layer with modified degradation rate on top of plough layer if evidence of photolysis is available OR Reduce application rate by the fraction that on average will disappear by photolysis in field degradation studies, provided that photolysis is a loss process in laboratory studies and that under the actual use conditions soil will be exposed to global radiation or photoradicals	
7.1.3	Anaerobic degradation	Degradation rate	Modify degradation rate in saturated soil layers if evidence of anaerobic degradation occurs	Includes subsoil degradation
7.1.4	Field degradation rates	Degradation rate	Use normalised degradation rates obtained from field studies	see FOCUS kinetics guidance (FOCUS, 2006)
7.1.5	Degradation kinetics not described by first order	Degradation rate	Consider non-equilibrium sorption approaches if possible. If the behaviour cannot be explained by non-equilibrium sorption an alternative bi-phasic approach may be appropriate	see Section 7.1.6 and FOCUS kinetics guidance (FOCUS, 2006)
7.1.6	Non-equilibrium sorption	K_d, K_f N	Introduce time dependent sorption constants	
7.1.7	Plant uptake	Transpiration stream concentration factor	Consider substance specific uptake factors	
7.1.8	Volatilisation	Degradation rate	Include a thin soil layer with modified dissipation rate on top of plough layer or switch on the model supplied volatilisation subroutines	

7.1.1 Soil specific sorption and degradation

Aerobic degradation is modelled in Tier 1 using first order degradation kinetics. Guidance on scaling degradation parameters in terms of moisture and temperature is given in FOCUS (2000, 2006). In many cases, a clear relationship may exist between the first order degradation constant and the soil properties. Indeed, if the degradation process is a microbiologically mediated process, a possible strong relationship between degradation rate and organic matter content in the soil may occur. Degradation rate will also depend on the bio-availability of the chemical in the soil liquid phase and hence will be influenced by the sorption properties which in turn are influenced by the reactive properties (CEC, charge, pH, etc…) of soils. If clear evidence of considerable soil effects on degradation exist, and if the soil conditions which determine such effects are readily shown to occur and if these soil conditions are representative for the envisaged protection goal, then these soil conditions can be incorporated explicitly in refinements of the degradation rates based on robust and quantifiable soil effects.

The standard FOCUS leaching scenarios take into consideration a depth dependent degradation rate by multiplying the surface degradation rate with 0.5 for the second soil layer and 0.3 for the deepest soil layer (FOCUS, 2000). Such degradation reduction deeper in the soil profile reflects the reduction of biotic activity deeper in the soil profile. The modification of degradation rate constants deeper in the soil profile is justified if evidence is provided for specific compounds.

Another example is the dependency of degradation rates on soil CEC, bulk density and soil texture (in particular percentage of clay), which relates to the bio-availability of substances to aerobic micro-organisms responsible for degradation, and which reflects the effect of soil sorption on degradation rates. If clear relationships exist between degradation rates and soil properties, than these relationships can be incorporated at Tier 2a.

The various models have different options for defining sorption and degradation that can vary with soil properties.

7.1.1.1 Degradation parameters and soil properties

In each of the FOCUS ground water models (PEARL, PELMO, PRZM, and MACRO), first order kinetics is used to describe degradation. The user supplies rate constants for the first soil horizon and then the programs calculate the degradation rate in each soil horizon. The user also has the option of specifying the rate constants for each soil layer. The degradation

rate in a specific soil horizon is constant for a run, but unless specified to the contrary is adjusted for soil moisture and temperature.

7.1.1.2 Sorption parameters and soil properties

7.1.1.2.1 MACRO

The user specifies the K_{oc} at reference conditions and Freundlich exponent and the program calculates the K_f values for each layer. The Freundlich exponent is a single value for the whole profile. MACRO 5 can model non-equilibrium sorption kinetics with a two-site model. Kinetic parameters are assumed to be constant for the whole soil profile.

7.1.1.2.2 PEARL

PEARL has the following three options:

1. pH-independent. Sorption described only with K_{om}.
2. pH-dependent. Sorption described by pH, $K_{om,base}$ and $K_{om,acid}$ according to equation 7-1 below
3. user defined. The user has to supply the K_f for each layer

PEARL contains a description of the sorption of weak acids, which is pH dependent:

$$K_{F,eq} = m_{om} \frac{K_{om.eq,ac} + K_{om,eq,ba}\dfrac{M_{ba}}{M_{ac}}10^{pH-pKa-\Delta pH}}{1+\dfrac{M_{ba}}{M_{ac}}10^{pH-pKa-\Delta pH}} \qquad (7\text{-}1)$$

where m_{om} is the organic matter content, $K_{om,eq,ac}$ (m^3 kg^{-1}) is the coefficient for sorption on organic matter under acidic conditions, $K_{om,eq,ba}$ (m^3 kg^{-1}) is the coefficient for sorption on organic matter under basic conditions, M (g mol^{-1}) is molar mass, pKa is the $^{-10}$log(KA) where KA is the dissociation constant, and ΔpH is a pH correction factor.

See Leistra et al. (2001) for the derivation of Equation 7-1.

7.1.1.2.3 PELMO

PELMO has the following four options:

1. pH-independent. Sorption in soil described based on K_{oc} only.
2. pH-dependent mode 1 (K_{oc} is known at a single pH). PELMO considers pH-dependency of sorption for weak acids. Equilibrium conditions between the non-ionic and the ionic form are calculated based on the pKa value. PELMO assumes that the sorption of the compound can be expressed by the weighted mean of the two species according to Equation 7-2:

$$K_{oc} = f_{H\text{-}A} * K_{oc,H\text{-}A} + (1-f_{H\text{-}A}) * K_{oc,A^-} \qquad (7\text{-}2)$$

K_{oc}:   sorption constant of the compound (L/kg)
$f_{H\text{-}A}$:   fraction of the non-ionic form in soil (pH-dependent)

$K_{oc,H-A}$:   sorption constant of the non-ionic form of the compound (L/kg)
$K_{oc,A-}$:   sorption constant of the ionic form of the compound (L/kg)

In mode 1 a constant Koc ratio of 1000:1 between non-ionic and ionic form of the compound is assumed. In mode 1 PELMO is <u>extrapolating</u> pH-dependent sorption constants.

3. pH-dependent mode 2 (K_{oc} is known at two different pH values). The same assumptions are assumed for the distribution of non-ionic and ionic form of the molecule. However, the ratio of the sorption coefficients between ionic form and non-ionic form is calculated compound specific based on two Koc-values given by the user. In contrast to mode 1 PELMO is therefore usually <u>interpolating</u> pH-dependent Koc for the range given by the user.

4. user defined. The user has to enter the sorption constant (K_{oc}) for each layer.

7.1.1.2.4 PRZM

PRZM has the following two options:

1. pH-independent. Sorption described only with K_{oc} at reference conditions and Freundlich exponent. The exponent is constant throughout the soil profile. The program calculates the K_f values for each layer.

2. user defined. The user has to supply the K_f values for each layer and the Freundlich exponent. The exponent is constant throughout the soil profile.

7.1.2 Photolytic degradation

If photolysis is significant then, as suggested by FOCUS (2006), degradation kinetics could be simulated by using the photolysis degradation rate in the soil near the surface (i.e. the first compartment of the soil model or for the first millimetre) and the non-photolytic degradation rate in deeper layers. Usually, the photolysis process is significant only in the time between application and the first rain (or irrigation) event after the application because the pesticide will be transported to deeper soil layers where it will not be affected by sunlight any more.

Another practical option to consider the loss by soil photolysis would be to determine the fraction that on average will disappear by photolysis in the field degradation studies (e.g. as a fast phase of a biphasic decline line), provided that photolysis was is proven as a loss process in laboratory studies and under the actual conditions the soil will be exposed to global radiation or photoradicals.

7.1.3 Soil specific anaerobic degradation

Anaerobic degradation is not currently explicitly addressed in the FOCUS models. The aerobic degradation term that is used as input is internally adjusted by the model depending on the calculated soil moisture within the profile (using the "Walker" equation; see FOCUS, 2002) but this does not extend to anaerobic conditions. The PEARL and MACRO models have a cut-off which prevents the moisture correction fraction from exceeding 1 (i.e. in the case that the calculated soil moisture in the soil profile exceeds the reference value of pF2) and the hydrology modules in PELMO and PRZM do not permit soil moisture to exceed the

reference value of pF2). Flooding (anaerobic conditions) in topsoil are generally not anticipated to last for significant periods and even these periods would be during the winter months when only limited pesticide application or residual pesticide activity is expected. Therefore, in the overwhelming majority of cases, the incorporation of a specific anaerobic degradation term for the topsoil is not necessary.

For sub-surface degradation (to a depth of 1m), the FOCUS models contain default factors relating the degradation rate to that in the topsoil (see Generic guidance for FOCUS groundwater scenarios, version 1.1, April 2002). If experimental anaerobic degradation data suggest specific mechanisms occur for a particular pesticide, for instance if degradation is chemically mediated and/or catalysed by the presence of Fe2+ oxides (Smelt et al., 1995), this may form a basis of a justification for amending these default values. This is in accordance with the existing FOCUS guidance (see FOCUS, 2002). Otherwise, the use of a specific anaerobic degradation term for the 30-100 cm soil profile is not considered necessary.

Evidence also exists that degradation may occur beyond 1 m in saturated zones. Leistra and Smelt (2001), for example, have shown that the presence of fossil organic carbon may sustain degradation in the subsoil. If degradation is chemically mediated and catalysed by the presence of Fe2+ oxides e.g., then the degradation may increase in reduced ground water where Fe2+ oxides are present (Smelt et al., 1995). Reductive dechlorination and methanogenic dechlorination have also been shown to be the transformation pathways for chlorinated substances in other anaerobic systems (Boesten et al., 1992; Van der Pas et al., 1998). Compound-specific anaerobic degradation data may be useful in predicting the degradation of a compound below 1 m (the default assumption in the FOCUS process is that no degradation occurs below 1 m).

7.1.4   Use of field dissipation degradation rates in leaching models

Field dissipation trials have been conducted for a number of compounds as a requirement under 91/414 or pertinent U.S. EPA or Canadian guidelines.

A clear advantage of field over laboratory results is that they are determined under conditions specific for the intended use of a pesticide in an agricultural field (i.e. unsieved soil, fluctuating soil temperature and moisture conditions, and often the presence of crops) and thus may closely match the situation which is to be modelled. Field DegT50 and DegT90 values also reflect the variation in degradation due to seasonal changes in climatic conditions. As a consequence degradation rates for parent and metabolites derived under

realistic field conditions may be used in pesticide fate modelling. This general recommendation implies that the design of the sampling regime excluded any significant route of dissipation other than degradation (for example, leaching, runoff, volatilisation, and plant uptake; see FOCUS, 2006).

In a strict sense, field dissipation degradation rates reflect primarily the degradation of a compound under site-specific soil and climate conditions. As a consequence averaging field degradation rates from different climate zones is not appropriate. To overcome this limitation FOCUS (2006) proposed two methods to normalize the results of field dissipation trials to a reference temperature of 20°C and a reference soil moisture of 100 % FC. After the normalization to reference conditions field dissipation data can be used in simulation models which account for the effects of temperature and soil moisture on degradation rates. Furthermore averaging normalized field dissipation half-lives from various climate zones (e.g. Northern and Southern Europe) as done with laboratory half-lives, is also appropriate. This principle may also apply to field dissipation trials from the U.S. and Canada if these trials were conducted in regions that are relevant for Europe. When using non-European field data, a short justification must be provided as to why the respective region is deemed representative for Europe. Some areas, like the sub-tropical southeastern states of the U.S.A, may not be representative for Europe. Detailed guidance on this subject is beyond the remit of the group.

Note that normalized half-lives should be exclusively used as input parameters in models, which are able to simulate daily variations of temperature and soil moisture. The normalized field half-life represents a half-life at 20 °C and 100 % FC (which is assumed to be reached at 10 kPa) whereas the uncorrected half-life reflects local temperature and soil moisture conditions.

FOCUS (2006) provided a detailed guidance on the two methods of normalisation of field half-lives. These recommendations should be followed when using field half-lives in FOCUS leaching models.

7.1.5   Degradation kinetics that deviate from first order
Degradation of compound in soil may not be suitably described in all cases with single first order kinetics models. In these cases non-equilibrium sorption approaches in FOCUS models with linked sorption and degradation routines (see Section 7.1.6) should be checked to see if they are capable of describing the behaviour of the compound and therefore suitable

for use in predicting leaching to ground water. Information on this subject is also given in FOCUS (2006) (see especially Section 7.1.2.2.1 and Appendix 4).

7.1.6   Non-equilibrium sorption

Another option for pesticide parameter refinement is to include non-equilibrium sorption. Long term sorption kinetics has been observed in many pesticide sorption experiments and has a significant impact on pesticide fate and transport. Wauchope et al. (2002) in their review on sorption distinguish three time scales for sorption kinetics of pesticides in soil: (i) minutes, (ii) hours (until a day or two), (iii) weeks to years. The process at a time scale of weeks to years is probably caused by slow diffusion of dissolved chemicals towards the sorption sites within soil pores or organic matter polymers (pore diffusion and intraorganic matter diffusion; see Pignatello, 2000).

7.1.6.1   Models for describing non-equilibrium sorption

A popular model for dealing with sorption kinetics is the two-site/two-region model (Van Genuchten and Wagenet, 1989; Streck et al., 1995), which separates the soil sorption sites in equilibrium and non-equilibrium sites. The basis for this simplification is that sorption sites reacting at time scales ranging from minutes to a day or two are close enough to equilibrium when assessing pesticide leaching to ground water. A two-site model is available in FOCUS PEARL (Leistra et al., 2001) and in MACRO 5.0 (Larsbo and Jarvis, 2003).

To describe non-equilibrium sorption, two types of additional parameters are necessary: the parameters describing the sorption isotherm of the non-equilibrium sites and a parameter describing the adsorption/desorption rate of these sites. The most relevant models for describing long-term sorption kinetics in the context of pesticide registration are described below.

7.1.6.1.1   PEARL

The submodel used in PEARL for sorption and degradation can be described as follows (Leistra et al., 2001):

$$c* = \theta\, c_L + \rho(S_{EQ,PEARL} + S_{NE,PEARL}) \tag{7-3}$$

$$S_{EQ,PEARL} = K_{F,EQ}\, c_{L,R} \left(\frac{c_L}{c_{L,R}}\right)^N \tag{7-4}$$

$$\frac{dS_{NE,PEARL}}{dt} = k_{d,PEARL}\left(K_{F,NE}\, c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^N - S_{NE,PEARL}\right)$$

(7-5)

$$K_{F,NE} = f_{NE,PEARL}\, K_{F,EQ}$$

(7-6)

$$R_t = -k_t(\theta\, c_L + \rho\, S_{EQ,PEARL})$$

(7-7)

where

$c^* =$ total concentration (mg/L)

$c_L =$ concentration in the liquid phase (mg/L)

$c_{L,R} =$ reference concentration in the liquid phase (mg/L)

$\theta =$ volume fraction of water (-)

$\rho =$ dry bulk density (kg/L)

$S_{EQ,PEARL} =$ content sorbed at equilibrium sites (mg/kg)

$S_{NE,PEARL} =$ content sorbed at non-equilibrium sites (mg/kg)

$K_{F,EQ} =$ equilibrium Freundlich sorption coefficient (L/kg)

$K_{F,NE} =$ non-equilibrium Freundlich sorption coefficient (L/kg)

$N =$ Freundlich exponent (-)

$k_{d,PEARL} =$ desorption rate coefficient (d^{-1})

$f_{NE,PEARL} =$ factor for describing the ratio between the non-equilibrium and equilibrium Freundlich coefficients in PEARL (-)

$R_t =$ rate of degradation in soil (mg L^{-1} d^{-1})

$k_t =$ degradation rate coefficient (d^{-1})

So the total Freundlich sorption coefficient $K_{F,tot}$ is defined in PEARL as follows

$$K_{F,tot} \equiv K_{F,EQ} + K_{F,NE} = \left(1 + f_{NE,PEARL}\right)K_{F,EQ}$$

(7-8)

As follows from Equation 7-3, the total content sorbed in the PEARL model, S_{PEARL}, is defined as:

$$S_{PEARL} \equiv S_{EQ,PEARL} + S_{NE,PEARL}$$

(7-9)

Equation 7-7 implies that pesticide sorbed at the non-equilibrium sorption site is not subject to degradation. As will be demonstrated below, mathematical analysis shows that including transformation at this site makes no difference for the description of long-term sorption kinetics (and thus makes also no difference for the leaching endpoint of the risk assessment).

For that purpose a model is considered (based on Equation 7-5) in which additionally first-order transformation occurs at the non-equilibrium site:

$$\frac{dS_{NE,PEARL}}{dt} = k_{d,PEARL}\left\{K_{F,NE}\ c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^N - S_{NE,PEARL}\right\} - k_{t,NE}S_{NE,PEARL} \tag{7-10}$$

where

$k_{t,NE}$ = rate coefficient for transformation at non-equilibrium sorption site (d^{-1}).

Equation 7-10 can be rewritten as:

$$\frac{dS_{NE,PEARL}}{dt} = (k_{d,PEARL} + k_{t,NE})\left\{\left[\frac{k_{d,PEARL}}{k_{d,PEARL} + k_{t,NE}}\right]K_{F,NE}\ c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^N - S_{NE,PEARL}\right\} \tag{7-11}$$

Effective values of $k_{d,PEARL}$ and $K_{F,NE}$ are now defined as follows (Boesten, 1986, p. 161):

$$k_{d,PEARL}^{eff} \equiv k_{d,PEARL} + k_{t,NE} \tag{7-12}$$

$$K_{F,NE}^{eff} \equiv \left[\frac{k_{d,PEARL}}{k_{d,PEARL} + k_{t,NE}}\right]K_{F,NE} \tag{7-13}$$

Thus Equation 7-11 can be rewritten as:

$$\frac{dS_{NE,PEARL}}{dt} = k_{d,PEARL}^{eff}\left\{K_{F,NE}^{eff}\ c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^N - S_{NE,PEARL}\right\} \tag{7-14}$$

Equation 7-14 is mathematically identical to Equation 7-5. So if first-order transformation occurs at the non-equilibrium site and Equation 7-5 is used for fitting, this process has already been included in the fitted $k_{d,PEARL}$ and $K_{F,NE}$ values. So this analysis shows indeed that including transformation at the non-equilibrium site makes no difference. Note that transformation at the non-equilibrium site leads to higher apparent $k_{d,PEARL}$ values and lower apparent $K_{F,NE}$ values.

7.1.6.1.2 The model of Streck

The model of Streck et al. (1995) defines the total concentration sorbed, S_{STRECK}, as follows:

$$S_{STRECK} = f_{EQ,STRECK}S_{EQ,STRECK} + (1 - f_{STRECK})S_{NE,STRECK} \tag{7-15}$$

where

$f_{EQ,STRECK}$ = the fraction equilibrium sites (-).

In this model the equilibrium content sorbed is defined as

$$S_{EQ,STRECK} = K_{F,tot} \, c_{L,R} \left(\frac{c_L}{c_{L,R}} \right)^N \qquad \text{(7-16)}$$

with $K_{F,tot}$ as defined by Equation 7-8. The sorption rate equation for the non-equilibrium sites is as follows:

$$(1 - f_{EQ,STRECK}) \frac{dS_{NE,STRECK}}{dt} = \alpha_{STRECK} (S_{EQ,STRECK} - S_{NE,STRECK}) \qquad \text{(7-17)}$$

where

α_{STRECK} = sorption rate coefficient (d^{-1}).

Comparison of Equation 7-15 with Equation 7-9 shows the following relationships:

$$S_{EQ,PEARL} = f_{EQ,STRECK} S_{EQ,STRECK} \qquad \text{(7-18)}$$

$$S_{NE,PEARL} = (1 - f_{EQ,STRECK}) S_{NE,STRECK} \qquad \text{(7-19)}$$

Using Equations 7-18 and 7-19, $S_{EQ,STRECK}$ and $S_{NE,STRECK}$ can be eliminated from Equation 7-17 Comparison of the resulting equation with Equation 7-5 leads to the following relationships between the parameters in the model used by Streck et al. (1995) and the parameters used in the PEARL model:

$$k_{d,PEARL} = \frac{\alpha_{STRECK}}{1 - f_{EQ,STRECK}} \qquad \text{(7-20)}$$

$$f_{NE,PEARL} = \frac{1 - f_{EQ,STRECK}}{f_{EQ,STRECK}} \qquad \text{(7-21)}$$

Note that Equations 7-20 and 7-21 are based on the theory and the model descriptions by Streck et al. (1995) and Leistra et al. (2001). Therefore, these equations are only valid in practice if the same operational definition of "equilibrium" is used (see Section 7.1.6.2 on experimental procedures).

7.1.6.1.3 MACRO

The submodel used in MACRO 5.0 (Larsbo and Jarvis, 2003) is based on the model of Streck but it uses a slightly different formulation of the rate equation:

$$\frac{dS_{NE,MACRO}}{dt} = \frac{\alpha_{MACRO}}{f_{NE,MACRO}} \left(K_{F,tot}\, c_{L,R} \left(\frac{c_L}{c_{L,R}} \right)^N - S_{NE,MACRO} \right) \qquad (7\text{-}22)$$

where

$S_{NE,MACRO}$ = content sorbed at non-equilibrium sites in MACRO (mg/kg)

α_{MACRO} = desorption rate coefficient (d^{-1}) used in MACRO.

$f_{NE,MACRO}$ = fraction of the non-equilibrium sorption sites in MACRO (-)

α_{STRECK} is identical to α_{MACRO} and it can also be shown that:

$$f_{NE,MACRO} = 1 - f_{EQ,STRECK} \qquad (7\text{-}23)$$

The relationships between the PEARL and MACRO parameters can be shown to be as follows:

$$f_{NE,MACRO} = \frac{f_{NE,PEARL}}{1 + f_{NE,PEARL}} \qquad (7\text{-}24)$$

or

$$f_{NE,PEARL} = \frac{f_{NE,MACRO}}{1 - f_{NE,MACRO}} \qquad (7\text{-}25)$$

and

$$\alpha_{MACRO} = k_{d,PEARL} \frac{f_{NE,PEARL}}{1 + f_{NE,PEARL}} \qquad (7\text{-}26)$$

or

$$k_{d,PEARL} = \frac{\alpha_{MACRO}}{f_{NE,MACRO}} \qquad (7\text{-}27)$$

In MACRO 5.0, the total sorption coefficient $K_{F,tot}$ is denoted as ZKD.

The above analysis shows that all three models are mathematically identical, and that parameters derived using one of the models can be translated into parameters of the other two models.

7.1.6.1.4 PRZM and PELMO

In the versions of PRZM and PELMO released with the new scenarios, non-equilibrium sorption is implemented as well. In both models the approach of PEARL as shown in

7.1.6.1.1 is used. However, in PELMO the parameters can also be inserted according to the Streck-model as shown in 7.1.6.1.3. The values are then internally converted according to Equations 7-20 and 7-21.

7.1.6.2 *Experimental procedures for measuring long-term sorption kinetics and procedures for estimating the model parameters*

The most straightforward procedure would be to measure long-term kinetics as part of the standard degradation rate studies. Measurements of long-term sorption kinetics have to be based on the total content of pesticide in soil because there is usually some degradation on a time scale of weeks. As a consequence the same or similar organic-solvent extraction procedures have to be used for measuring (i) the degradation rate and (ii) long-term kinetic parameters. This can be illustrated with the following example. Mild extraction procedures (e.g. single extraction with ethyl acetate or acetone) will lead to shorter half-lives than strong extraction procedures. Strong extraction procedures (e.g. soxhlet extraction or repeated extractions with different types of solvents) will lead to higher contents sorbed at the non-equilibrium site.

The parameters for the equilibrium site should be derived from the standard adsorption experiments. These experiments have an equilibration time of typically 24 h which corresponds well with the time scales of the first two types of site as defined by Wauchope et al. (2002). We use the symbol $K_{F,ads,batch-1day}$ for a Freundlich sorption coefficient measured in an adsorption batch experiment of about one day (OECD, 2000). An additional advantage is that these are also the parameters used in previous lower tiers. The parameters for the non-equilibrium site should be derived from incubations of moist soil because this is closest to field conditions. We will call such studies hereafter 'aged sorption studies'. Those studies are very similar to laboratory soil degradation studies according to OECD guideline 307 (OECD, 2002). One may expect that batch sorption experiments on time scale of weeks lead to an overestimate of the $k_{d,PEARL}$ (i.e. the rate coefficient of the non-equilibrium sites) because of the shaking procedures in such experiments.

Leistra et al. (2001) recommend to measure the equilibrium sorption coefficient in PEARL ($K_{F,EQ}$) via a standard batch experiment (so $K_{F,EQ} = K_{F,ads,batch-1day}$). So if the true total Freundlich coefficient $K_{F,tot}$ is available, $f_{NE,PEARL}$ can be estimated as:

$$f_{NE,PEARL} = \frac{K_{F,tot} - K_{F,ads,batch-1day}}{K_{F,ads,batch-1day}} = \frac{K_{F,tot}}{K_{F,ads,batch-1day}} - 1 \qquad (7\text{-}28)$$

As described before, Equations 7-19 and 7-20 are based on the theory and the model descriptions by Streck et al. (1995) and Leistra et al. (2001). However, these publications recommend different operational definitions for measuring the equilibrium and the rate of exchange of the non-equilibrium sorption sites. Although Equations 7-19 and 7-20 are mathematically correct, they are of little use when these different operational definitions are used. Streck et al. (1995) propose to measure the rate coefficient α_{STRECK} by shaking a soil suspension over a period of about a week. This implies that the equilibrium sites in the Streck model equilibrate within a time period in the order of 1 h. However, Leistra et al. (2001) propose to measure $k_{d,PEARL}$ in aged sorption studies that may last a few months. Furthermore, the operational definition for the equilibrium sites of Leistra et al. (2001) is shaking for about 1 day in a batch study. Thus if the recommendations of Streck et al. (1995) and Leistra et al. (2001) are followed, a consistent operational value for $f_{NE,PEARL}$ from results obtained by the Streck approach, can be obtained from Equation 7-28 where $K_{F,tot}$ is derived from fits based on the Streck approach.

Measurement of long-term kinetics in moist soil requires a time series of:
  (i) the total content of pesticide in soil.
  (ii) the concentration of pesticide in the soil pore water.

The concentration in the pore water can be measured by collecting liquid phase (e.g. centrifuge a soil sample over a filter). This will not work for all soil types. An acceptable alternative is to perform a 24-h desorption experiment and to assume that (i) the equilibrium sorption site is at equilibrium after these 24 h and (ii) the change in content sorbed at the non-equilibrium site is negligibly small over these 24 h shaking time. The concentration in the pore water can then be back calculated using the difference between the solid-liquid ratios of the moist soil and the batch desorption systems or can be directly fitted if the model is able to calculate the concentration in the suspension solution with a given soil:water ratio.

Alternatively, non-equilibrium sorption parameters can also be obtained from controlled (steady) pesticide column leaching experiments. Analytical solutions for the two site-two region models have been developed by Toride et al. (1993), and have been readily implemented in the CXTFIT model identification tool (1995). Yet, inverse modelling of pesticide breakthrough for identifying sorption kinetic parameters may be inappropriate or subjected to a lot of uncertainty (Vanderborght et al., 1997). The parameters for the equilibrium sorption site also in this case should be based on independent batch experiments with a shaking time of 1 day. If breakthrough curves were inversely modelled and residual concentrations in the soil column at the end of the column study have been measured, it is

preferable to include these results in the inverse modelling procedure. More details on inverse modelling are given in Chapter 8.

Estimating non-equilibrium sorption parameters from lysimeter leachate concentrations may also be possible. However, probably this is only possible in exceptional cases because other system properties may have an effect on the pesticide breakthrough that is similar to the effect of non-equilibrium sorption parameters.

Another option would be to estimate non-equilibrium sorption parameters from field experiments that include desorption studies from soil samples from the top centimetres. So far little experience is available with this procedure. More experience with such procedures should be gained before using them in risk assessments.

Theoretically, non-equilibrium sorption parameters may be derived from analysis of adsorption-desorption hysteresis as performed by Streck et al 1995 and Altfelder 2000 using the FITHYST fitting tool (Streck 1997). Using this approach the total sorption $K_{F,tot}$ can be estimated; using Equation 7-28 $f_{NE,PEARL}$ can then be estimated if an independently measured value of $K_{F,ads,batch-1day}$ is available. Although the relevance of the estimated parameters were tested by comparing the so-derived parameters with other experimental data (Streck, 1995, Streck, 1999, Altfelder, 2001, Jene, 2007), more information is necessary to derive non-equilibrium sorption parameters using this method.

Finally, sorption kinetic parameters may also be estimated from analysing bi-phasic degradation kinetics. Indeed, the occurrence of bi-phasic degradation kinetics may be the macroscopic expression of the microscopic non-equilibrium sorption. Guidelines for estimating long term sorption parameters for PEARL from bi-phasic kinetic degradation experiments are given by FOCUS (2006). However, this procedure is expected to work only in cases in which the degradation rate of the first phase is very fast (half-lives in the order of 5 days).

7.1.6.3 Overview of available measurements of long-term sorption parameters

There are many studies demonstrating the significance of the long-term sorption process (e.g. see data for Hawaiian soils cited by Hamaker & Thompson, 1972, and for a UK soil measured by Walker, 1987). However few experiments have been analysed with the submodels used by PEARL or MACRO. Boesten et al. (1989) found $f_{NE,PEARL}$ values ranging from 0.3 to 0.4 and $k_{d,PEARL}$ values ranging from 0.01-0.02 d^{-1} for cyanazine and metribuzin in a sandy soil. They showed that the assumption of non-equilibrium sorption was necessary to

explain the movement of the substances in a field experiment. Boesten and Gottesbüren (2000) found a $f_{NE,PEARL}$ value of 0.55 and a $k_{d,PEARL}$ value of 0.015 d^{-1} for bentazone in a sandy soil. Using the same bentazone data, Tiktak et al. (2000) found $f_{NE,PEARL}$ =0.73 and $k_{d,PEARL}$ =0.019 d^{-1}. Boesten (personal communication, 1996) found a $f_{NE,PEARL}$ value of 0.75 and a $k_{d,PEARL}$ value of 0.005 d^{-1} for both metamitron and hydroxychlorothalonil in a sandy soil. Based on this information Leistra et al. (2001) recommend to use a default f_{NE} value of 0.5 and/or a default k_d value of 0.01 d^{-1}. Gurney and Hayes (2007) analysed a herbicide where aged sorption studies were carried out in three soils yielding $f_{NE,PEARL}$ values of 0.42, 0.48 and 0.75. They did not estimate the sorption rate coefficient $k_{d,PEARL}$ but fixed it to the default value of 0.01 d^{-1}. Jene (2006) reported an average $f_{NE,PEARL}$ value of 2.7 for a pesticide based on aged sorption studies with two soils. So this $f_{NE,PEARL}$ value is much larger than the other values that have been reported. However field degradation studies with the same compound at seven sites showed extreme bi-phasic behaviour which could be well explained by applying the non-equilibrium sorption concept using the high $f_{NE,PEARL}$ values from the laboratory study.

There is also indirect evidence for the long-term sorption process. Streck et al. (1995) showed that the leaching of simazine in a field lysimeter transport experiment could be explained if non-equilibrium sorption estimated from sorption hysteresis data of a laboratory batch sorption study was considered in the modelling. In Streck and Richter (1999) the depth concentration profile of chlortoluron in a field leaching study could only be reproduced by modelling if the kinetic parameters derived from the sorption batch experiment where used. Finally, Altfelder et al. (2001) showed the compatibility of the results from laboratory batch adsorption and column experiments with regard to the non-equilibrium sorption behaviour of dimethylphtalate.

Indirect evidence can also be derived from the hysteresis phenomenon. Hysteresis in adsorption/desorption isotherms measured in batch systems has been reported in many publications. Altfelder et al. (2000) demonstrated for a few studies that the observed hysteresis could be explained by long-term adsorption kinetics using the FITHYST software package (Streck, 1997) which is based on the model of Streck et al. (1995). In one example the 24-h adsorption isotherm had a value that was only 50% of the 'true' equilibrium isotherm, so $f_{NE,PEARL}$ was about 1.0. Studies by Pignatello and co-workers have shown that part of the observed hysteresis is not related to long-term sorption kinetics but to a 'true' change in the sorption equilibrium caused by an irreversible deformation of the organic matter (e.g. Sander et al., 2005).

Reichenberger et al. (2002) analysed adsorption-desorption isotherms of 8 pesticides (in total 67 studies) with the FITHYST software package and found a median ratio of the quotient $K_{F,tot}$ / $K_{F,ads,batch-1day}$ of 1.79 which implies a median $f_{NE,PEARL}$ of 0.79 (See Equation 7-28). The poster-version of their paper showed a very large scatter in this quotient. Reichenberger et al. (2002) did not provide the source of the 67 studies but probably all data sets comprised at least two desorption steps and a study of adsorption kinetics following procedures described in OECD guideline 106. Reichenberger and Laabs (2003) analysed adsorption-desorption isotherms for nine pesticides and two tropical soils. They derived $K_{F,tot}$ values from experiments on adsorption kinetics on a time scale up to 4 days and from experiments with five sequential desorption steps that lasted in total 7 days. They found a median value of the quotient $K_{F,tot}$ / $K_{F,ads,batch-2days}$ of 1.6 and 2.4 for the two soils (so $K_{F,EQ}$ was defined by 48 h shaking). The range of the quotients was considerable (from 0.7 to 12) and the average value was 3.0 and 3.6 for the two soils. The median values correspond with f_{NE} values of 0.6 and 1.4 for the two soils. However, no standard deviations were provided for estimated $K_{F,tot}$ values. It cannot be excluded that these values have a large uncertainty; e.g. a value of the quotient $K_{F,tot}$ / $K_{F,ads,batch-2days}$ of 12 implies that the $K_{F,tot}$ based on experiments that lasted at most 7 days is 12 times higher than the adsorption coefficient measured after 2 d shaking. Such an increase is very unlikely.

Reichenberger and Laabs (2003) found a median value of the rate coefficient α_{STRECK} of 0.05 d^{-1} for both soils and median f_{STRECK} values of 0.4-0.5. This means that they found $k_{d,PEARL}$ values in the order of 0.1 d^{-1}, which is an order of magnitude higher than the $k_{d,PEARL}$ values found in moist soil by Boesten et al. (1989), Boesten and Gottesbüren (2000) and Tiktak et al. (2000). This difference is probably caused by the shaking procedure used in batch adsorption-desorption measurements which leads to faster equilibration than would occur in field soils.

Jene (personal communication, 2004) analysed adsorption-desorption measurements in soil suspension for one pesticide and seven soils and found ratios of the quotient $K_{F,tot}$ / $K_{F,ads,batch-1day}$ of 3.1 to 6.6 (so $f_{NE,PEARL}$ values of 2.1 to 5.6).). For one of those values ($f_{NE,PEARL}$ of 2.2), which was derived from a lysimeter soil, Jene (2007) could show that almost the same value was estimated when fitting the outflow behaviour of this pesticide from three replicated outdoor lysimeters.

The $f_{NE,PEARL}$ values found in adsorption-desorption batch experiments by Altfelder et al. (2000), Reichenberger et al. (2002), Reichenberger & Laabs (2003) and Jene (personal communication, 2004) tend to be higher than those found in aged sorption studies. However,

no studies are available where $f_{NE,PEARL}$ is measured both via adsorption-desorption isotherms and via aged sorption studies for the same pesticide-soil combination. Given the limited number of $f_{NE,PEARL}$ values that are available, no conclusion is yet possible on the relationship between $f_{NE,PEARL}$ values measured with both methods. The possibility cannot be excluded that $f_{NE,PEARL}$ values obtained from adsorption-desorption isotherms are systematically higher than those obtained from aged sorption. This may lead to overestimation of $K_{F,NE}$ if $f_{NE,PEARL}$ values derived from FITHYST estimates are used in combination with $K_{F,NE}$ values based on measurements of $K_{F,ads,batch-1day}$.

Other indirect evidence is the frequently observed phenomenon that aged pesticides residues are more difficult to extract than fresh pesticide residues (see e.g. Smith, 1981). To the best of our knowledge there is no evidence in the opposite direction (i.e. demonstrating that long-term kinetics did not occur when carefully studied for pesticides with significant adsorption).

7.1.6.4 *Recommended default values for long-term sorption parameters in risk assessment*

In conclusion, the considerable amount of direct and indirect evidence for a long-term kinetic sorption process makes defensible the use a default $k_{d,PEARL}$ value of 0.01 d^{-1} and a default $f_{NE,PEARL}$ value of 0.3 (and the equivalent values $f_{NE,MACRO} = 0.231$ and $\alpha_{MACRO} = 0.00231$ d^{-1}). The $k_{d,PEARL}$ of 0.01 d^{-1} is the 'best guess' for the rate coefficient based on available measurements in aged sorption studies and the $f_{NE,PEARL}$ of 0.3 is a realistic worst-case estimate based on the lowest value found in an aged sorption study. The lowest value is chosen because of the limited amount of data available and because it includes implicitly also all variation in organic solvent extraction procedures for degradation rate studies in the laboratory and field.

The recommended default values should only be overruled by compound-specific values measured in aged sorption studies (either incubation studies or column leaching studies as described above) because batch experiments may give $f_{NE,PEARL}$ values that are systematically higher than those found in aged sorption studies. This recommendation might change when more information becomes available on the comparison between long-term sorption parameters measured in aged sorption studies and in adsorption-desorption batch experiments.

To overrule these default values, aged sorption studies with at least two soils are needed. The $k_{d,PEARL}$ and $f_{NE,PEARL}$ values found for the different soils should be averaged to obtain the

arithmetic mean. If data for only one soil are available, the default $f_{NE,PEARL}$ value of 0.3 should be used in the averaging procedure for the other soil.

7.1.6.5 Fitting of aged sorption measurements to long-term kinetic sorption parameters
When fitting of results of aged sorption studies, the equilibrium Freundlich sorption coefficient, $K_{F,EQ}$, should be taken from batch experiments with the same soil using OECD-106 if available. In a number of cases, batch adsorption isotherms will not be available for the soils considered in the aged sorption studies. In such cases, the kinetic model should be used to fit the parameter $K_{F,EQ}$ (i.e. $K_{F, ads, batch-1day}$). In practice this means that this parameter value is mainly based on the desorption point measured after 0 or 1 day equilibration. The alternative would be to fix this parameter using the average K_{OM} from the available batch adsorption isotherm studies. However, then the kinetic model cannot describe accurately the course of time of the concentration in the liquid phase in the first days of the aged sorption study which will give less reliable values of the long-term kinetic parameters.

An example how to derive non-equilibrium sorption parameters by using different available tools is given in Appendix 6. Fitting non-equilibrium sorption parameters is more or less a new field of science in which so far there is limited experience. Often expert judgement will be needed with respect to the interpretation of the data. As a minimum quality requirement, the 95% confidence intervals of fitted parameters should be within the range from 0 to 200% of the fitted value to be acceptable.

The kinetic sorption model itself is already a unique description of the dynamics applied. However it can be expressed in several ways using different variables to be used as target or object function by an optimisation algorithm (i.e. fitting tool). The basic measurements in a typical (laboratory) aged sorption study are the concentration in the supernatant after desorption and centrifugation and the amount extracted by organic solvents, the sum of which is the total extractable mass. Both measurements contain a mixture of the phases as defined in the kinetic sorption model above. The concentration in the supernatant includes the dissolved and a part of the equilibrium sorbed mass before the desorption (because the desorption step led to desorption of part of the adsorbed substance). The mass extracted by organic solvents contains the non-equilibrium sorbed mass and residues of the other phases. Thus there are two alternative possibilities to set up the target function. The first is to let the model fit directly the measured quantities, i.e. the concentration in the supernatant as dissolved concentration (c_L) and the total mass. The second approach is to start with calculating back the concentrations (c_L, S_{EQ}, S_{NE}) in the sample before the desorption from

the measurements and performing the fit on these concentrations. Both approaches should in principle give the same results.

Weighting of data is a complicated issue because there are two types of measurements that have to be fitted: total mass (or total content) in soil and concentration in the liquid phase. If for instance the absolute values of the total content are several times higher than the liquid phase concentrations, the fit will be dominated by the total mass values and only marginally influenced by the liquid phase concentrations, although the liquid phase concentrations may equally important for the non-equilibrium sorption.

FOCUS (2006) provided guidance for fitting of degradation rates. The report states on p. 71: "Unweighted fitting to data often results in a better overall fit of SFO kinetics due to lower sensitivity to deviations of calculated from observed data in the later stages of dissipation. In laboratory experiments, these deviations may be due to the influence of increasing sorption and/or decreasing microbial activity." Moreover FOCUS (2006) states: "Logarithmic transformation may be justified if there is experimental evidence that smaller concentrations can be determined with greater precision than larger values. Otherwise, unweighted fitting to untransformed data is recommended." This cannot be interpreted as support for using unweighted fitting for aged sorption studies because the aim of the optimisation process for aged sorption studies differs from the aim for fitting SFO degradation rates. The most important difficulty for aged sorption studies is that fitted values for the $k_{d,PEARL}$ and $f_{NE,PEARL}$ parameters are regularly very unreliable (e.g. 95% confidence intervals exceeding 100% of the estimated value). Thus considerations to achieve a more reliable fit of $k_{d,PEARL}$ and $f_{NE,PEARL}$ may overrule considerations to achieve the best fit of the *DegT50*. Given the limited knowledge in this field a case-by-case approach is recommended with testing of different weighting options and a justification of the selected option.

For an appropriate interpretation of the quality of the fit, the following graphs have to be included in any report determining non-equilibrium sorption parameters:
- comparison of measured and fitted total concentration of pesticide in soil as a function of time
- comparison of measured and fitted concentration of pesticide in soil pore water or in soil suspension (depending of what was measured) as a function of time
- comparison of (i) measured concentration of pesticide in soil pore water or in soil suspension (depending of what was measured) as a function of time and (ii) calculated concentration in soil pore water or soil suspension assuming SFO and the equilibrium sorption parameters.

7.1.6.6 Consequence of using non-equilibrium sorption for the degradation rate to be used in simulation models

Both in PEARL and well as in MACRO, PRZM, and PELMO (optionally), degradation is restricted to the equilibrium sorption phase. So if non-equilibrium sorption is included in model calculations, the consequence is that all degradation rate studies have to be re-evaluated as well, assuming the same set of long-term kinetic parameters for all degradation rate studies (so $k_{d,PEARL}$ = 0.01 d^{-1} and $f_{NE,PEARL}$ =0.3 when using the default values). The re-calculation procedure depends on the kind of studies (laboratory or field degradation studies) and the kind of the substance (parent or metabolite).

The symbol $DegT50_{tot}$ is used for the conventional $DegT50$ that is based on a rate considering the total pesticide content in soil and the symbol $DegT50_{eq}$ is used for the $DegT50$ that is based on only pesticide present in the equilibrium phase in soil (as described by Equation 7-7). Figure 7-1 illustrates the difference in definition between $DegT50_{tot}$ and $DegT50_{eq}$. $DegT50_{eq}$ is linked only to the liquid phase and the equilibrium sorption sites, whereas $DegT50_{tot}$ applies to the whole soil, including the long-term sorption sites. If no non-equilibrium sorption is defined (as in default in Tier 1 calculations), DegT50$_{tot}$ is equal to DegT50$_{eq}$.
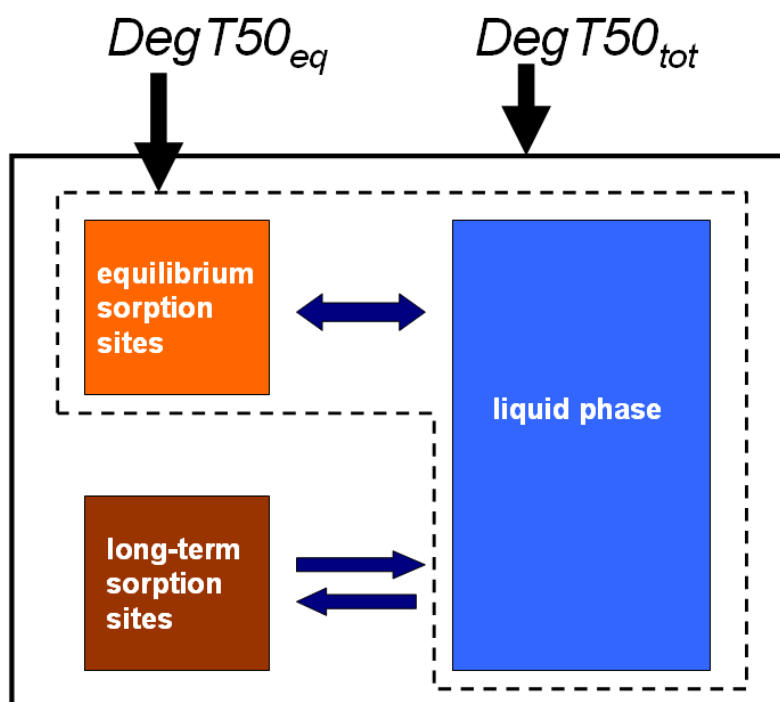
Figure 7-1. Diagram showing how _DegT50_$_{tot}$ and _DegT50_$_{eq}$ are linked to the three different phases in soil (_DegT50_$_{eq}$ being linked only to the liquid phase and the equilibrium sorption sites, whereas _DegT50_$_{tot}$ applies also to the long-term sorption sites). The double headed arrow indicates equilibrium and the two separate arrows symbolise adsorption/desorption rates

In order to re-calculate _DegT50_ values of ordinary laboratory degradation studies for the use in a non-equilibrium sorption simulation, one of the model systems (e.g. MACRO or PEARL) that can be used for non-equilibrium parameter estimation should be applied. The non-equilibrium sorption parameters ($f_{NE,PEARL}$ and $k_{d,PEARL}$ or $f_{NE,MACRO}$ and α_{MACRO}) should be fixed to the values derived from the evaluation of the aged sorption studies or the default values ($k_{d,PEARL}$ = 0.01 d^{-1} and $f_{NE,PEARL}$ =0.3). The re-calculated _DegT50_, which now only represents the degradation in the equilibrium sorption phase of the soil, can only be used in the simulation models together with the corresponding non-equilibrium sorption parameters. Appendix 7 presents an example of how to calculate _DegT50_$_{eq}$ when the default non-equilibrium sorption parameters are assumed.

In order to use the non-equilibrium sorption in simulation models such as PEARL and MACRO for PEC$_{gw}$ calculations, the re-scaled, shorter _DegT50_$_{eq}$ - value must only be used in combination with the non-equilibrium sorption parameters with no degradation in the simulated non-equilibrium sorption phase. If the non-equilibrium sorption rate parameter

$k_{d,PEARL}$ or α_{MACRO} is zero or the parameter describing the fraction of the non-equilibrium sorption phase $f_{NE,PEARL}$ or $f_{NE,MACRO}$ is set to zero, non-equilibrium sorption is not considered in the model and the $DegT50_{tot}$ (so not the shorter $DegT50_{eq}$) must be used.

For metabolites that were tested in parent studies (laboratory or field) a pragmatic approach could be to follow the procedure used in Boesten and Van der Linden (2001). This means that the degradation of a metabolite would be simulated according to the estimated rate derived from the parent study (where non-equilibrium sorption was not considered). Then the simulated total concentrations were fitted with a non-equilibrium sorption model where the non-equilibrium sorption parameters as well as the sorption equilibrium parameter were fixed and only the degradation rate in the equilibrium sorption phase was fitted. Equations 7-29 to 7-31are given here only for obtaining a first guess of the magnitude of the difference between DegT50$_{tot}$ and DegT50$_{eq}$. They should not be used in risk assessment procedures.

Boesten and van der Linden (2001) derived an approximation for the scaling factor f_{deg_NE} which can be used to obtain a first guess for the magnitude of the difference between $DegT50_{tot}$ and $DegT50_{eq}$). The scaling factor is defined as:

$$f_{\deg,NE} \equiv \frac{DegT50_{eq}}{DegT50_{tot}}$$

(7-29)

or

$$DegT50_{eq} \equiv f_{\deg,NE}\, DegT50_{tot}$$

(7-30)

The approximation assumes a linear sorption isotherm and assumes that the degradation rate coefficient is slow compared to $k_{d,\,PEARL}$. The approximation can be written as:

$$f_{\deg,NE} = \frac{w + K_{F,EQ}}{w + (1 + f_{NE,PEARL})K_{F,EQ}}$$

(7-31)

where w is the gravimetric water content of the incubation system defined as volume of water divided by mass of dry soil (L/kg). Using e.g. $w = 0.2$ L/kg, $K_{F,EQ} = 1$ L/kg and $f_{NE,PEARL} = 0.5$, gives $f_{deg\_NE} = 0.7$, so the effect on the estimated $DegT50$ value may be considerable.

7.1.7   Plant uptake

The default plant uptake factors (i.e. the transpiration stream concentration factor) can be adjusted to measured values if substance specific uptake factors have been determined in appropriate experiments.

7.1.8   Volatilisation

If volatilisation is significant then, degradation kinetics could be simulated by using the volatilisation rate in the soil near the surface (i.e. Include a thin soil layer with modified dissipation rate on top of plough layer or switch on the model-supplied volatilisation subroutines) and the "in-soil" degradation rate in deeper layers.

7.2   Scenario refinement (Tier 2b)

In Tier 2b scenario refinements are suggested to improve the initial Tier 1 simulations. In principle, all model input parameters except product specific parameters (for example, K_{oc}, DegT50) or application patterns could be considered within this tier.

The overall purpose of Tier 2b is to allow modifications of the existing Tier 1 scenarios in order to define "product specific" scenarios based on the specific use pattern of the pesticide.

Table 7-2 gives an overview of relevant aspects that can be considered for the proposed scenario refinements. Some more details are given in the following sections.

Table 7-2. Overview of refinements included in Tier 2b.

Section	Aspect	Related Parameters	Proposed Refinement	Remarks
7.2.1	Specific crop conditions	Crop parameters	Modification of crop parameters in terms of known soil and climate properties	Considering alternative methods to define more accurate dates for emergence, maturation or harvest
7.2.2	Specific crop conditions	Crop rotation	Definition of realistic crop rotations instead of permanent crops	Especially for pesticides that are not used on an annual basis
7.2.3	Specific crops	Crop type	Definition of additional crops not covered by FOCUS tier 1	Improvement of simulations for pesticides that are used mainly in special crops with minor importance ("niche products")
7.2.4	Specific use pattern	Crop, climate	Definition of scenarios for greenhouse applications	The current focus scenario do not cover greenhouse applications
7.2.5	General definition of "product-specific"-scenarios based on GIS. Tier 2.2a because the FOCUS scenario is replaced completely	All scenario parameters could be affected	Exclusion of areas that are not relevant with respect to the use pattern of pesticides	Identification of characteristic combinations of • crops • climate conditions • soil types • ground water conditions • hydro-geological information
7.2.6	Specific irrigation scenario	Climate parameters	Modify irrigation rates to consider implementation of more efficient drip irrigation	

7.2.1   Modification of crop parameters

In Tier 1 the crop parameters (not only root depth, emergence, maturation and harvest dates, but also runoff related parameters) are constant for each scenario. However, especially the crop development parameters vary within the major agricultural areas due to the influence of climate and also to some extent soil parameters. Additional information on the location of the cropping areas and special crop parameters could be used to refine the Tier 1 simulations; resulting in more realistic simulations for specific crops and excluding climate/soil/crop-combinations that do not occur in reality.

7.2.2   Introduction of realistic crop rotations

Whether pesticides are applied annually or at other frequencies, crop rotations are never considered within Tier 1 simulations. Instead, all crops are assumed to be cultivated as

"permanent crops". A refinement can be considered by introducing location dependent crop rotations in Tier 2b. If, for example, a certain pesticide is used every third year only in potatoes only, additional crops could be defined for the years without any application. Since the selection of crops has an important influence on the water regime, as a consequence the fate of pesticide residues in the soil also will be affected by these refinements.

The original FOCUS input files cannot be used for these simulations. The user must always create specific input files for this refinement, and the process for running these input files depends on the simulation model selected. When combining different crops within simulations, the user should start with the official FOCUS crop development dates (emergence, maturation, harvest) rather than defining completely new figures. The warming up period of 6 years was defined for annual, biennial and triannial application patterns only, but the 6 years warming up period should also be maintained for other rotations.

7.2.3   Introduction of new crops

Tier 1 covers only the major European crops. If pesticides are modelled that are primarily used for minor crops (e.g. special fruits or vegetables) the user has to select a similar major crop. However, at Tier 2b a more realistic solution would be to develop a scenario for this minor crop.

A cautionary remark should be made for rice cropping, which cannot be considered a minor crop. Agricultural practice for rice cropping is completely different than for other classical agriculture crops. The work group believes that current standard FOCUS pesticide leaching models and scenarios can not be used for assessing risk in rice cultivated crops. For rice cropping, interested readers are referred to the MED-Rice (2003) report.

7.2.4   Specific use conditions (e.g. greenhouse scenario)

Tier 1 scenarios are only designed to assess pesticide leaching in arable land subjected to traditional pesticide management (e.g. spraying of chemicals using traditional spraying equipment). Specific pesticide uses can be considered e.g. for greenhouses which may justify the modification of the climate and soil parameters, the introduction of specific "greenhouse" crop parameters and the modification of the timing and rate of pesticide applications. EFSA has begun a project in this area "New Guidance on Protected Crops" (greenhouses or cultivations grown under cover).

7.2.5   Defining use specific scenarios (e.g. use of GIS)

The FOCUS Tier I scenarios apply to large climatic zones (Chapter 11). In many cases, plant protection products will only be applied in part of these climatic zones, particularly in the

case of minor crops that are grown in only a confined area. If the FOCUS scenarios are not specific enough for the intended use, the notifier may wish to develop a scenario that is specific for the intended use, i.e. for the relevant combination of crops, soil types, climate and ground water conditions. The development of these so-called 'use specific scenarios' is the subject of this section. The procedures in this section result in completely *new* scenarios, which may complement existing FOCUS scenarios for specific uses in higher-tier calculations.

GIS approaches play an important role in the development of new scenarios. Soil information is combined with other spatial environmental and agricultural data (climate patterns, crop, distribution, hydrogeological data) by spatially overlaying basic maps using Geographic Information Systems (GIS). Such an overlay results in a large number of possible scenarios (in many cases more than 1000), all which need to be parameterised. If spatial information is available with sufficient detail, a spatially distributed model can be created. The PECgw can be selected directly from the cumulative frequency distribution of the calculated concentrations.

In many cases sufficient soil information for running spatially-distributed models is not available. Therefore, a simplified leaching concept is required in cases where insufficient soil and climate data is available. In these cases, the simplified leaching model is applied to the intended use area instead of the spatially-distributed model itself (see Appendix 5 for more details). If parameterised in an appropriate way, this simplified leaching model results in a leaching vulnerability map that shows a strong correspondence to the leaching map obtained with the spatially distributed model itself. This offers the opportunity to select the target scenario directly from the frequency distribution of the calculated concentrations obtained with the simple model. This single scenario is assigned parameter values (horizon designations, organic matter content, texture, hydraulic properties etcetera) and a FOCUS leaching model is run for this single scenario to generate the intended leaching concentration.

In summary:
- Spatially-distributed modelling comes down to running a large number of scenarios with a FOCUS leaching model and presenting the results in a map and a cumulative spatial leaching distribution (Tier 3b).
- Modelling with use specific scenarios comes down to run a simplified leaching model, identify the 80th percentile vulnerable location from the map and calculate the regulatory endpoint for this single scenario (Tier 2b).

In those cases where sufficient soil and climate information is available to parameterize a process-based spatially distributed model, this is the preferred method. In all other cases use-specific scenarios would be the better choice although they are the second best alternative. For this reason, spatially-distributed modelling is put at a higher tier (Tier 3) than modelling with use-specific scenarios, which is a Tier 2 approach.

7.2.5.1 Steps in applying use-specific scenarios

The development and application of use specific scenarios at Tier 2b can be structured in five major steps, i.e.

1. data compilation, check for suitability and data quality;
2. ground water vulnerability mapping using a simplified leaching concept
3. scenario selection;
4. scenario parameterization;
5. simulation with a FOCUS leaching model.

The leaching in Tier 2b is assessed twice: first with the simplified leaching model to identify areas which comply with the preset vulnerability criterion (i.e. step 2), and secondly to assess the regulatory end point (step 5). This process is illustrated in Figure 7-2. The individual steps are shortly described below; a more detailed guidance and examples are given later in this section.

7.2.5.1.1 Data compilation, check for suitability and data quality

Appendix 8 gives an overview of pan-European spatial data bases and spatial data bases on a member state level that can be used for the development of new scenarios for EU-registration. For national registration, the use of national data bases is preferred, if they have a higher resolution and are of better quality than EU data bases. For those cases where national data bases are missing or of insufficient quality, the data bases referred to in Appendix 8 can be used for the development of Tier 2 scenarios as well.
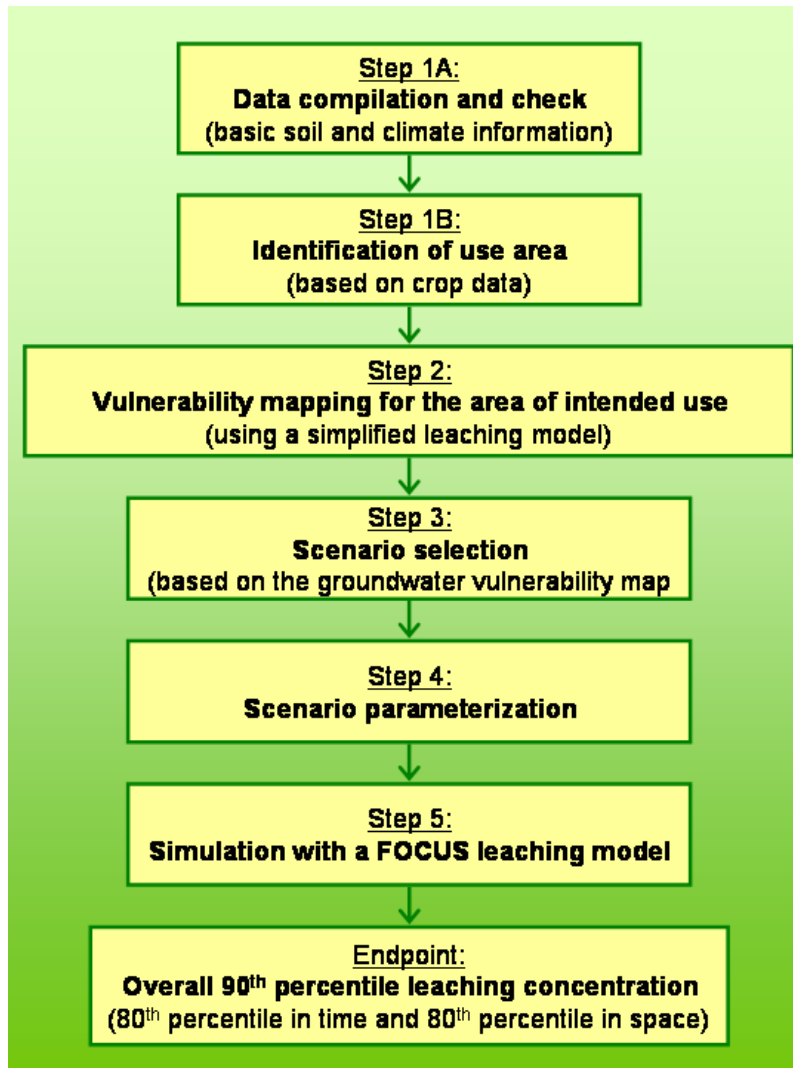
Figure 7-2. Illustration of the process to develop use specific scenarios at Tier 2b. Crop data refers to the distribution of crops.

7.2.5.1.2 Vulnerability mapping using a simplified leaching concept

In this step, a simplified leaching model is run to get a ground water vulnerability map. The modelling should be done for the area of intended use. A large number of simple leaching concepts is available in the literature (Aller et al., 1987; Jury et al., 1983; 1987; Jury and Roth, 1990; Loague et al., 1989, 1996; Loague and Corwin, 1996; Rao et al., 1985; Douven, 1996; Vanclooster et al., 2003; Stewart and Loague, 2003; 2004; Piñeros Garcet et al., 2006; Hollis and Sweeney, 2006; Stenemo et al., 2006; Tiktak et al., 2006). The work group describes two different approaches in detail (Appendices 4 and 5); other approaches were not explicitly excluded but have not been evaluated in detail by the work group.

7.2.5.1.3 Scenario selection

During this step, grid cells are selected that meet the target vulnerability. For EU-registration, the target vulnerability is about the 80th percentile in space and 80th percentile in time. Individual member states may, however, use different target vulnerabilities. The Netherlands, for example, use the 90th percentile in space and the 50th percentile in time. Both approaches are approximations of the overall 90th percentile vulnerability. The selection of grid cells can be done directly from the cumulative frequency distribution of the generated maps. The target vulnerability should apply to the intended use area only.

7.2.5.1.4 Scenario parameterization

Once a use-specific scenario location is selected, an appropriate parameterisation of soil and climate is needed. If runoff is important in the use area, runoff should also be included. Also during this phase, several choices have to be made. First, soil profile data need to be assigned on the basis of the selected soil mapping unit. This is not a trivial step, because detailed soil information is not always available. Once a soil profile is found, derived data such as the bulk density and the hydraulic characteristics of the soil profile must be parameterized as well. These data are usually not available in soil profile data bases, but must be derived by so-called pedotransfer functions. With respect to hydraulic properties, several pedotransfer functions are available (Wösten et al., 1994; Schaap et al., 1998; Wösten et al., 1999). A complete review of the pedotransfer functions was beyond the scope of this work group. Runoff can be calculated using mechanistic approaches, as done in, for example, PESERA (Kirby et al., 2004). The current FOCUS ground water models, however, lack an appropriate description of some of the important processes relevant to the generation of overland-flow, particularly surface crusting. Therefore, the work group recommends the use of the more empirical NRCS curve number method, but care should be taken not to include runoff originating from sources that are less relevant to pesticide leaching such as saturation excess runoff originating from partial contributing areas (Richards and Brenner, 2004; Garen and Moore, 2005). One pragmatic way to deal with this is to assign an adjusted USDA hydrological group through HOST (Hydrology Of Soil Types) attributes.

7.2.5.1.5 Simulation with a FOCUS leaching model

During this step, PECs are calculated with a standard FOCUS leaching model (i.e. MACRO, PEARL, PELMO or PRZM).

7.2.5.1.6 Precautionary remark

As shown before, the development of new scenarios requires a large number of choices to be made. All these choices result in uncertainty and subjectivity. First, a leaching model

must be chosen and parameterized for scenario selection. This may result in different locations of the selected scenario. Also during the scenario parameterization phase, choices have to be made. Therefore, all steps must be reported in a transparent way so that they can be reviewed by the national registration authorities. This requires that all data that are used for scenario generation are available to all stakeholders free-of-charge or for administrative costs only. Finally, the consistency of the selected scenario within the tiered assessment scheme should be checked as well. If this is not possible directly, then the method used to develop the scenario should be evaluated in a reference area, where sufficient data is available to parameterize a process based numerical model.

7.2.5.2   Detailed guidance

7.2.5.2.1   Data compilation and quality check

Appendix 8 gives an overview of pan-European spatial data bases that can be used for the development of new scenarios for EU-registration. Appendix 8 also provides procedures to improve the quality of the spatial data bases. For new national scenarios, the use of national data bases should be considered, because they may have a higher resolution and better quality. For those cases where national data bases are missing or of insufficient quality, the pan-European data bases referred to in Appendix 8 can be used for the development of national scenarios as well. References of spatial data bases used (with their main characteristics, including scale and spatial resolution) must be described with the selection of the scenario.

7.2.5.2.2   Vulnerability mapping using a simplified leaching concept

In this step, a simplified leaching model is run to generate a ground water vulnerability map. The work group agreed that methods to derive the ground water vulnerability map should:

- reflect the vulnerability criterion as being a concentration with a spatial distribution;
- be consistent amongst the tiers (later tiers must be more realistic and earlier tiers must be more conservative than later tiers);
- cover ideally the entire area of the EU, so that they are applicable for both national and European procedures (harmonization, more efficient registration).

The leaching models differ in their data needs and in the way how the data are processed. In accordance to what has been found in the literature, the following four types of models can be distinguished:

- *Process based numerical models:* Leaching concentrations or loads are calculated using process oriented leaching concepts. Numerical models solve the differential

equations describing pesticide fate and transport for transient boundary conditions and complex initial conditions. All FOCUS leaching models (PEARL, PELMO, PRZM and MACRO) fall into this category. Most approaches to spatially-distributed, process based numerical modelling come down to running a leaching model for several (often more than 1000) scenarios and putting the results in a map. This kind of process based numerical leaching models can be parameterized for the catchment scale (Petach et al., 1991; Leterme et al., 2007a), the regional scale (Capri et al. 2000), the national scale (Tiktak et al., 1996; 2002) and the European scale (Tiktak et al., 2004). Notice that only few attempts to model the transport of pesticides into the deeper ground water have been reported in the literature (Tiktak et al., 2005).

- *Analytical, process based models:* Analytical models are analytical solutions of the differential equations, describing pesticide fate and transport in soil subjected to simple initial and boundary conditions. The best known models of this type are the attenuation factor (Loague et al., 1989; 1996; Loague and Corwin, 1996) and the transfer function (Jury and Roth, 1990; Stewart and Loague, 2003; 2004). Analytical models that are not calibrated to results from numerical models (see below) can only be used as screening tools (Loague and Corwin, 1996; Stewart and Loague, 2004; Tiktak et al. 2006).

- *Meta-models of process-based models:* Meta-models reduce the complexity of process based numerical models, but maintain the essential behaviour of the complex model by considering the sensitivity of the different attributes in the spatial assessment. Regression analysis can be used to construct a meta-model (Figure 7-3). The regression model can itself be a purely statistical model (Vanclooster et al., 2003; Stenemo et al., 2006; Piñeros Garcet et al., 2006) or a combination of a simplified process based model and a regression model (Van der Zee and Boesten, 1991; Stewart and Loague, 2004; Tiktak et al., 2006).

- *Index rules:* Attribute data that control leaching are combined in a simple logical rule and corresponding arithmetic rules (mostly linear combination of attributes or parameters) to yield a vulnerability index. Weights can be assigned to different attributes in terms of the sensitivities of individual parameters to leaching. The DRASTIC model (Aller et al., 1987; Lobo-Ferreira and Oliveira, 1997) assigns weights based on expert judgement. Weights can also be based on the sensitivity of a process-based model. In this way, process information is implicitly incorporated in the index and the index-rule becomes a metamodel of a process-oriented model. Appendix 4 gives an example of such an approach.
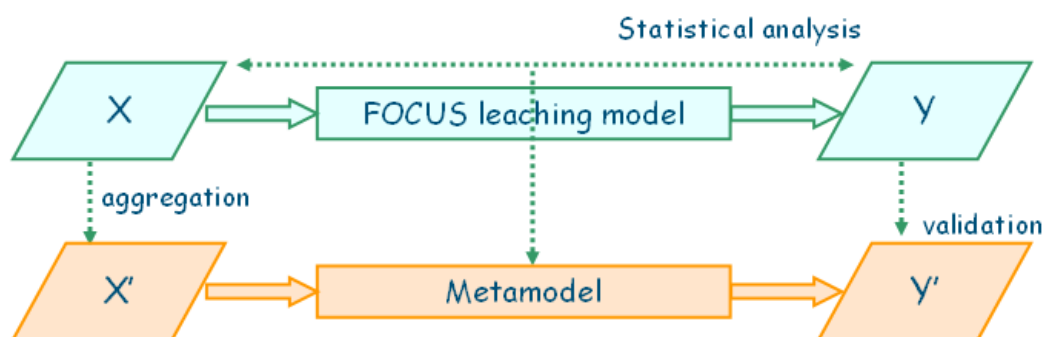
Figure 7-3. Metamodels are proxies of complex models

The work group concluded that metamodels and index rules are the best choice for scenario development in Tier 2b, because these approaches are compatible with data in pan-European data bases. Two examples of these approaches are described in detail. Appendix 4 describes an index rule, based on organic matter, precipitation and temperature. Appendix 5 describes a process based metamodel of the recently developed pan-European pesticide leaching model EuroPEARL (Tiktak et al., 2004; 2006). Process based spatially distributed models are considered less suitable for Tier 2b assessments, because so far they cannot be parameterized for the entire area of the EU (Tiktak et al., 2004). They may, however, be the best choice in certain situations, particularly if a high quality national data base is available (Tiktak et al., 2002). In those cases, the regulatory endpoint can be selected directly from the frequency distribution of the generated leaching maps, so that the development of use specific scenarios is not necessary. Spatially-distributed modelling is therefore recommended for Tier 3.

Spatially-distributed models can also be seen as the reference for simple leaching models, because the spatially distributed models use the FOCUS leaching model directly. A benchmark of the simple leaching concept against a process based model should be carried out as part of the scenario development (or reference should be made to earlier attempts to benchmark the simple leaching concept). An important element of this benchmark should be the correlation between the maps generated with the process based model and the simple model. The benchmark should preferably be carried out against a spatially distributed model based on a FOCUS leaching model, such as GeoPEARL (Tiktak et al., 2002). This type of benchmark can only be carried out in regions where sufficient soil and climatic information is available. The two methods described by the work group meet this requirement, because they were both benchmarked against GeoPEARL for the Netherlands (see Appendix 9).

Appendix 9 also contains an analysis of strengths, weaknesses, and opportunities of the two approaches.

7.2.5.2.3 *Scenario selection*

The result of either of the two approaches is a map showing the leaching potential in a normalized way (i.e. the grid cell with the highest leaching potential scores 100% and the grid cell with the lowest leaching potential scores 0%). The target scenario can be selected directly from this map and corresponds to 80[th] percentile vulnerable location (for national registration, the target percentile may be different). Because the crop area is considered as an approximation of potential pesticide use, the crop area could be used as a weighting factor. See the documentation of GeoPEARL (Tiktak et al., 2003) for an example how the crop area can be included.

The two approaches described by the work group may result in different target scenarios. For this reason, the work group proposes to select a number of grid cells in the 85-95 percentile vulnerability range to deliver the candidate scenarios. An appropriate number of candidate scenarios must be selected and parameterized for the selected FOCUS leaching model. The FOCUS leaching model should be run with the selected scenarios and all PEC's should be reported. All scenarios should meet the trigger values to achieve a registration without further mitigation restrictions.

7.2.5.2.4 Scenario *parameterisation*

The GIS analyses described in Appendices 4 and 5 both yield areas for candidate scenarios. Since the regulatory endpoint is eventually calculated by a standard FOCUS leaching model, a soil and climate scenario must be developed for the selected location. The following section provides a generic but rough guidance on the parameterisation of soil and climate scenarios in the context of a FOCUS leaching assessment. The FOCUS leaching models contain a large number of model inputs. Guidance on the parameterization of the FOCUS leaching models is given in the user manuals of the individual models (PEARL, PRZM, MACRO and PELMO), the latest versions of these manuals and parameterisation documents are accessible through the FOCUS website.

In principle, all model inputs could be affected when building use-specific scenarios. The work group recommends, however, staying as close as possible to the parameterisation of the FOCUS scenario for the corresponding climatic zone (see FOCUS, 2000, and Chapter 12 for a description of these climatic zones). Particularly generic parameters that are considered independent of the FOCUS Tier 1 scenarios should not be changed.

7.2.5.2.4.1 Meteorological time-series

The MARS climate data base provides daily weather data for the entire EU in a 50 x 50 km^2 grid. Therefore, extracting weather files for the selected location from the appropriate grid cell is straightforward. The MARS data base contains all parameters that are required for simulation runs with current FOCUS models such as minimum and maximum temperature, rainfall, potential evapotranspiration, and global radiation. All weather files for Tier-1 FOCUS leaching scenarios were derived from this data base; therefore MARS should be used as the primary source for weather information in Tier 1. If possible, the weather data provided by MARS should be converted to a 66-years time-series using the rules described in FOCUS (2000). As discussed in Section 11.5.1, MARS reference evapotranspiration should be converted to FAO reference evapotranspiration in southern locations for consistency with the FAO crop kc factors.

The use of data from local weather stations may be considered in specific cases when notifiers attempt to simulate a very specific local weather situation or when sufficient evidence exist that MARS data for the considered region is biased. In view of the large geographic extent of most soil units in the EU soil data base, station data do not necessarily improve the spatial accuracy compared to weather data that was specifically derived for such larger scale assessments.

7.2.5.2.4.2 Cropping parameters

As a first approximation, most crop parameters (e.g. date of emergence, date of harvest, crop development stages, etc.) should be taken from the Tier 1 scenario of the corresponding climatic zone. See FOCUS (2000) or Chapter 13 in this report for a definition of these climatic zones. In some cases more detailed information on cropping dates exist, in particular when crops are grown in confined areas with characteristic climate conditions. In such cases modifying cropping dates or other parameters may be appropriate. When changing cropping parameters, a rationale for each change must be provided in order to ensure a high degree of transparency in the assessment. If scenarios are developed for minor crops, then a completely new cropping parameterisation may be required.

7.2.5.2.4.3 *Irrigation*

If irrigation is a relevant practice in the intended use area, the scenario has to be set up accordingly and typical irrigation amounts need to be assigned. If reported irrigation data are available, the data may be used directly in the parameterisation of the scenario. In most cases, such data are not available and irrigation amounts will have to be estimated. The compatibility of the irrigation data with the other climate data should be checked.

Typical crop water requirements during the vegetation period can be calculated on the basis of FAO methods and MARS data (Allen et al, 1998). The difference between crop water consumption and precipitation is then determining the irrigation demand. Note that the water storage capacity of soils is not considered when calculating crop water requirements on the basis of climate parameters. In these cases the calculated irrigation amounts might be higher than those applied in reality. This problem does not occur when calculating the irrigation demand with the soil water module within a FOCUS leaching model (for example SWAP in PEARL) so this approach is preferable. Section 11.5.3 describes how the FOCUS models were used to generate the irrigation schedules.

7.2.5.2.4.4 Lower *boundary* conditions

If detailed information on the local ground water regime is available, this information can be used to parameterize the lower boundary condition. If no information is available, then the parameterization of the FOCUS Tier I scenario in the corresponding climatic zone (FOCUS, 2000) could be used.

7.2.5.2.4.5 *Hydraulic* balance

The hydrological subroutines of the models should be parameterised in order to mimic the hydraulic balances for the scenarios as realistic as possible for the intended simulation areas. In other words, estimates of recharge at target depth should neither be significantly underestimated nor overestimated. For example, if runoff is thought to be a major process in the area of interest, runoff should be included. Runoff can be calculated using mechanistic approaches, as done in, for example, PESERA (Kirkby et al., 2004) The current FOCUS ground water models, however, lack an appropriate description of some of the important processes relevant to the generation of overland flow, particularly surface crusting. Therefore, the work group recommends using the NRCS curve number method, but care should be taken not to include runoff originating from sources that are less relevant to pesticide leaching such as saturation excess runoff originating from partial contributing areas (Richards and Brenner, 2004; Garen and Moore, 2005). One pragmatic way to deal with this is to assign an adjusted USDA hydrological group through HOST (Hydrology Of Soil Types) attributes. HOST uses pedotransfer rules to relate major flow pathways to generally available pedological information (Boorman et al., 1995). HOST was originally developed and validated in the UK, but is currently applied to the entire EU within the EU FOOTPRINT project (Dubus et. al., 2007). However, results of this project will not become available before the end of 2008, so the work group could not evaluate this approach.

7.2.5.2.4.6 Soil *parameters*

The parameterisation of the soil properties consists of three steps: (a) selection of a soil profile from a soil profile data base, (b) parameterisation of basic soil information, which is directly available in these data bases (usually horizon designations, organic matter, texture and sometimes also pH), and (c) parameterisation of derived soil properties that are not available in the soil profile data base (soil hydraulic functions, bulk density of the soil, etc.).

Step A: Selection of a soil profile. Soil profile data bases usually contain information on the soil mapping unit from which the soil profile originates. The link between the soil map and the soil profile data base is then a trivial step, because there is a 1:1 link. At the European level, however, this link is not straightforward. The problem is that the Soil Mapping Units (SMU's) at the EU-soil map are associations of dominant and subdominant Soil Typological Units (STU's). The STU's and not the SMU's are the carriers of basic soil information, such as the FAO soil name and the soil textural class. For this reason, the link between the soil map and the profile data base needs to be done in two steps. A possible approach could be to determine the dominant STU, and then assign a soil profile to this dominant STU. Notice that during this step information on subdominant soil profiles will be lost, leading to a possible bias during the assessment (Vanclooster et al., 2003). An additional problem is that the Soil Profile Analytical Database of Europe (SPADE, Madsen-Breuning and Jones, 1995) usually does not contain explicit information on the associated soil typological unit. Finally, many STU's at the EU-soil map do not have an associated soil profile. To overcome these problems, two approaches can be followed:

- The link can be made at a relatively low spatial resolution (for example the resolution of the MARS grid cells, which is 50x50 km^2). Such a large grid cell usually contains multiple soil mapping units, so that the chance of finding an STU with an associated soil profile increases. Notice that in this procedure, the selection of the dominant STU is not carried out at the level of soil mapping units, but at the level of these large grid cells. An example of this approach is worked out in Appendix 4.
- The second approach operates on the level of Soil Mapping Units and uses general pedological rules to establish the link ('class matching'). This method has often been used in pedological research (for example Van Orshoven et al., 1993; Leterme et al., 2007b). The method used here is based on the work done within the APECOP project and forms the basis of the EuroPEARL model (Tiktak et al., 2004). In this approach, a profile is assigned on the basis of the full FAO soil name, the textural class and the country code. Including the country code in the query assures that soil profiles from a given country could only be matched to Soil Mapping Units within that

country. In those situations where a link could not be established, the query was repeated with the full FAO soil name and the country code only. Finally, a query was carried out using the major soil type and the country code only (e.g. Cambisol instead of Eutric Cambisol). In a recent development, Hollis and Sweeney (2006) merged the soil typological units further, by assuming that a specific class of soil typological units can be used to represent the characteristic of that group anywhere in the EU. In other words, they did not use the country in their query. See Appendix 5 for more details.

The most important difference between the two procedures is that the first merges multiple soil mapping units and uses a relatively low *spatial* resolution, while the second approach merges soil types and uses a lower '*pedological'* resolution. The advantage of the first method is its relatively simplicity. A disadvantage is, however, that this procedure operates on a lower resolution than the soil mapping unit, which is the target unit for assessing the ground water vulnerability (cf. Section 10.1). Vanclooster et al. (2003) showed that the use of dominant values across large spatial blocks may cause bias in the leaching assessment.

Both methods result in the selection of a soil profile. When building the scenario, the suitability of the selected soil profile for the target crop should be evaluated. In particular, depth to parent material, pH, and texture give important indications whether the soil profile is likely to sustain a viable growth of the target crop. If the selected STU is outside the range of 'suitable soils', a soil typological unit with a lower coverage should be selected instead.

Step B: Parameterization of basic soil data. The Soil Profile Analytical Database contains information on horizon designations (thickness of soil profiles), organic matter, textural distribution and pH. The data in SPADE is not necessarily based on measurements, but are estimated profiles, meaning that national soil scientists have given a best possible description of typical soil profiles in their country. For this reason, the organic matter content in the upper 30 cm should be scaled to the organic matter content derived at the recently developed pan-European organic matter content map as published by the Joint Research Centre (Jones et al., 2004, 2005). In contrast to SPADE, this map has been validated against measured soil data in some reference areas.

SPADE-1 has some data gaps that need to be filled. In some cases, the properties of the subsoil are not given. A very critical parameter is the organic matter content. In those cases where organic matter content is not available, several approaches could be followed. Leterme et al. (2007a) suggest using the following empirical relationship:

$$OM(z) = OM_b + (OM_o - OM_b)\exp(-kz)$$

where z is the depth (cm); OM_o and OM_b are the organic matter contents in the top horizon and at the bottom of the soil profile, respectively; and k is a constant. If no information is available, OM_b should be set zero (conservative approach). Parameter k could be obtained from data in corresponding soil profiles.

Step C: Parameterization of derived soil data using pedotransfer rules. Bulk density and hydraulic properties are not available in SPADE. These parameters must therefore be derived by so-called pedotransfer functions. PEARL has a built-in function, which relates organic matter content to bulk density (Tiktak et al., 2000). Alternatively, Carsel et al. (1998) use the textural distribution to predict the bulk density. Parameter values for the Mualem-van Genuchten functions (van Genuchten, 1980) can be derived from the HYPRES data base (Wösten et al., 1999), but alternative approaches where the hydraulic function is estimated on the basis of advanced statistical procedures are available as well (Schaap et al., 1998). The water content at field capacity (required by PRZM and PELMO) can be directly derived from the above hydraulic functions.

7.2.5.2.5   Simulation with a FOCUS leaching model

Once the scenarios have been parameterized, the calculation of the endpoint can be done with a standard FOCUS leaching model.

7.3   References

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8   APPROACHES FOR TIER 3 ASSESSMENT

For Tier 3, four alternatives exist: First, a combination of strategies proposed in Tier 2; second, advanced spatial modelling approaches; third, higher tier leaching studies placed into context; and fourth, other modelling approaches.

8.1   Procedures for combining modelling based on refined parameters and scenarios (Tier 3a)

Where relevant to the proposed use pattern, the refinements detailed in Tiers 2a and 2b (see above) can be combined to provide an assessment based on both approaches.

The relationship of the compound's behaviour to certain soil properties or more realistic degradation or sorption parameters in combination with environmental scenarios more specifically adapted to the intended use pattern will provide a more realistic assessment of the leaching behaviour than if only a single option is used. This is seen as a further refinement of the assessment and hence supersedes Tier 2.

Only a general short description of combining modelling based on refined parameters and scenarios is given here due to the multitude of possible options of combined Tier 2a and Tier 2b approaches. The options at Tier 3a are likely to be used quite frequently at Tier 3 at EU and at national level.

8.2   Procedures for building a spatially-distributed FOCUS leaching model (Tier 3b)

This report describes two methods to introduce spatially-distributed data in the leaching assessment:

- In the first method, a simplified leaching model is applied to the intended use area. This model is used to generate a ground water vulnerability map. A single scenario representing the 80th percentile vulnerable location is selected from the so-obtained map. This scenario is than parameterised, and the FOCUS target is obtained with a standard FOCUS leaching model. This approach is called 'modelling with use-specific scenarios and is described in Section 7.2.5.

- In the second method, a spatially distributed version of a FOCUS leaching model is directly applied to the intended use area, and the regulatory endpoint can be calculated directly from the frequency distribution of the so-obtained leaching map. This can only be done in those cases where the soil and climate data cover the

intended use area (and are of sufficient quality). This method is described in this section (Section 8.2).

In those cases where spatially-distributed modelling is considered appropriate, this is the preferred method (see Section 8.2.1). In all other cases, use-specific scenarios would be the better choice although they are the second best alternative. For this reason, spatially distributed modelling is put at a higher tier (Tier 3) than modelling with use-specific scenarios, which is a Tier 2 approach.

8.2.1 Justification for spatially-distributed modelling

The agricultural and environmental parameters that affect pesticide fate and transport are variable in time and space. The resulting leaching event which charges ground water can therefore be considered as a stochastic variable, characterized by its probability density function (pdf). The elementary leaching event is thereby defined in space at the scale of the soil mapping unit and in time at the scale of a year. The leaching event pdf measures the variation of the elementary leaching event in a larger space area (corresponding in FOCUS to a climatic zone in Europe) and longer time period (corresponding in FOCUS to the simulation period of respectively 20, 40 or 60 years, not including the six year warm-up period). With the adopted vulnerability concept, the 90^{th} percentile of the leaching event pdf is selected as end point for regulation. In Tier 1, the pdf of the leaching event is not explicitly reconstructed but the appropriate percentile is inferred from the pdf of the temporal varying leaching event, given a percentile soil. However, this pragmatic lower tier approach may give a biased estimate of the 90^{th} percentile:

- Only one specific percentile soil is selected for a given climate area based on qualitative information of the soil variability and expert knowledge, without explicitly characterizing the variability of soil parameters contributing to the leaching event variability.
- The leaching event percentile is calculated from the temporal variable leaching event pdf, which is considered to be normally distributed. Extreme percentile estimates (e.g. 90^{th} percentile) assuming normal distributions for variables which effectively are nonnormally distributed may be extremely biased. The shape of the leaching event joint pdf in space and time is a-priori not known and may be skewed and exhibit high kurtosis.
- The leaching event correlation in space and time is ignored, given that the joint pdf in space and time is not explicitly reconstructed. Some underlying properties defining the leaching event pdf will be correlated in time. An example may be the activation of macro porous flow in macroporous soils, triggered by extreme rainfall events.

In the higher tier, this bias may be reduced by introducing explicitly spatial variation of the leaching event. Two different approaches may be distinguished:

- In a first approach the spatial variation of the underlying properties (soil, crop, climate, agricultural) driving the leaching event is considered as a basis for the selection of a more appropriate scenario. This scenario is next combined with a leaching model to assess the percentile of the leaching event. This is the approach proposed in Tier 2. As compared to Tier 1, this procedure results in a explicit characterization of the underlying properties and therefore an improved scientific basis for scenario selection. Examples of such a procedure have been given in Appendices 4 and 5.

- In a second approach, the spatial variation of the underlying properties driving the leaching event is also considered. Yet, in this approach the leaching event is calculated for each realisation of the underlying variable. Examples of such approaches are given in Tiktak et al., (2002; 2004a). Given the availability of spatially distributed leaching events, a percentile value can be selected a posteriori. This is the approach proposed in Tier 3, and is described further in this section.

The problem of the calculation of percentile values of a space-time variable is equivalent to problem of the aggregating and upscaling of point values to a larger support volume (Heuvelink and Pebesma, 1999). Given X, the set of space-time variables contributing to the leaching event; $L(X)$, the space-time variable leaching event; and $p()$ the procedure of selecting a percentile value; then it can be shown $L(p(X)) = p(L(X))$ is only applicable in limited cases (namely X is uniformly distributed and L is a linear model in X). In general, the calculated leaching event is considered to be a non-linear function of soil properties and therefore the above mentioned equality is not trivial. For instance Heuvelink and Pebesma (1999), showed that the calculation of a linear process model after the interpolation of underlying variables resulted in smaller errors as compared to the situation where the process model was calculated first. For a non-linear process models (such as the leaching models used in FOCUS), Leterme et al. (2007a) showed that opposite results may be obtained. The conclusions depend however on the resolution of the underlying data, the scale at which a prediction needs to be made, and the correlation of the underlying variables (in case of the FOCUS scenarios, the correlation between the soil, climate and crop parameters).

8.2.2   Development of a spatially distributed FOCUS leaching model

The most important steps in the development of a process-based spatially distributed FOCUS leaching model are described below. This discussion relies on the use of the

PEARL and GeoPEARL models, but other FOCUS leaching models could have been used as well:

1. Selection of an appropriate leaching model
2. Review of existing databases
3. Development of a spatial schematisation (i.e. derivation of the unique combinations by overlaying in a GIS basic maps)
4. Model parameterisation
5. Running the FOCUS leaching model and plotting the results in a map
6. Calculation of the target percentile

Each individual step is shortly described below. A more comprehensive description of the various steps and background information is given in Tiktak et al. (2002, 2003, 2004b).

8.2.2.1 *Selection of an appropriate leaching model*

In the context of the harmonised European pesticide registration procedure, four leaching models are currently being used, i.e. PRZM-3 (Carsel et al., 1998), PELMO (Klein, 1995), PEARL (Tiktak et al., 2000) and MACRO (Jarvis et al., 1991). All models are one-dimensional, dynamic, multi-layer models of the fate of a pesticide and relevant transformation products in the soil system. PELMO, PRZM-3 and PEARL are chromatographic flow models, while MACRO contains modules for calculating preferential flow. Basic soil information for preferential flow models such as quantitative soil structure information (Rawls et al., 1996) is not yet available in pan-European or national soil data bases. Despite recent developments in this area (Jarvis and Dubus, 2006), whether this information will become available soon is questionable. Preferential flow models are therefore not considered in this section.

8.2.2.2 *Review of existing databases*

Appendix 8 gives an overview of pan-European spatial data bases that can be used for building a spatially distributed pesticide leaching model. For national registration, the use of national databases is preferred, if they have a higher resolution and better quality. If national databases are missing, pan-European databases could be used as the second best alternative.

For building a set of pan-European spatially distributed pesticide leaching scenarios, soil, climate and cropping databases are needed. The MARS (climate) and Corine (land-use) databases cover the entire European Union. The Soil Profile Analytical Database of Europe, release I (Jamagne et al., 1995), however, has serious limitations. The most serious limitation is that only 75% of the agricultural area of the EU-15 could be assigned a soil

121

profile (Tiktak et al., 2004a, Figure 8-1). Also, in many cases, the assigned soil profile is not an agricultural profile. This implies that it is not yet possible to build a spatially distributed FOCUS leaching model, which covers the entire EU.
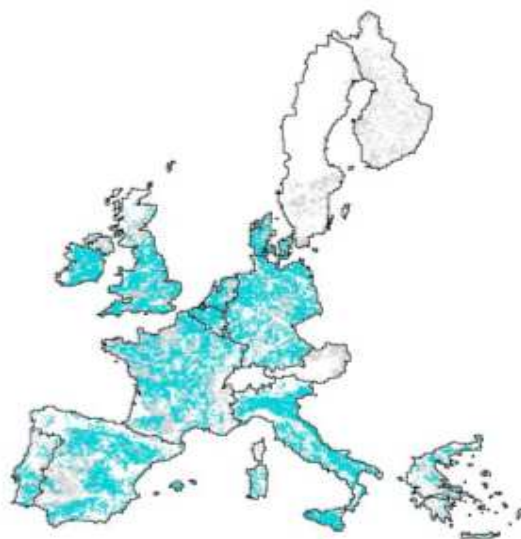
Figure 8-1. Only 75% of the agricultural area of the EU-15 could be assigned a soil profile (blue area)

At the national level, the situation can be different. Some countries (for example the Netherlands (Tiktak et al., 2002), Belgium and Germany (Bangert, 2007)) do have sufficient soil information available to build a spatially distributed FOCUS leaching model. This means that in these countries, the development of a spatially distributed FOCUS leaching model is possible.

8.2.2.3 Development of a spatial schematisation

In this step, unique combinations (also referred to as scenarios or plots) are defined by spatially overlaying maps of basic spatial attributes. We recommend transferring the basic maps into a grid environment before further processing, although the analysis can also be done in a polygon environment. A common resolution and projection must be chosen. The FOCUS target is defined on the level of soil mapping units (Section 11.1), so we recommended using a grid cell size that is compatible with the average size of soil mapping units on the available soil map. The EU soil map 1:1,000,000 justifies the use of a grid cell size of 10x10 km^2 (Jones, personal communication, 2003). By using a lower resolution, variability in organic matter will be averaged, leading to a possible bias in the final model predictions (Vanclooster et al., 2003; Leterme et al., 2007b).

The soil type and climatic class should always be considered when constructing the spatial schematisation. The user might, for example, want to overlay the 50x50 km^2 grid cells from the MARS climatic database with a national soil map. If additional spatial attributes are available, then these attributes can also be considered. For the construction of the GeoPEARL model for the Netherlands, Tiktak et al. (2002) included the ground water depth class and information about the subsoil into the spatial schematisation. In some countries, information about the presence of irrigation systems (Siebert and Döll, 2001) may be relevant as well. Information on the intended use area can be used as a mask after the overlay has been constructed.

The overlay may result in a large number of unique combinations. The construction of a spatially distributed model in the Netherlands, for example, resulted in 100,000 unique combinations. Because such a large number of unique combinations leads to unacceptable computation times, the number of scenarios must then be reduced. For this reduction, various techniques are available:

- the number of climatic classes or soil types could be reduced by combining MARS grid cells or soil types that have similar properties.
- unique combinations that represent a very small area could be eliminated.

How the overlay is done, and which technique is followed to reduce the number of unique combinations is largely dependent on the available data bases.

Example: The spatial schematisation for the EuroPEARL model
Tiktak et al. (2004a) constructed a pan-European pesticide leaching model, referred to as EuroPEARL. They constructed a spatial schematisation by overlaying the following two maps (Figure 8-2):

1. The 1:1,000,000 soil map of the European Union (Jamagne et al., 1995). This map features a total number of 735 Soil Mapping Units (SMU's). Each map unit is an association of Soil Typological Units (STU's) occurring within the limits of a discrete physiographic entity and is composed of a dominant soil type and of subdominant associated soils. Only those soil units that could be assigned a soil profile were considered (see Section 8.2.2.4.5).
2. A map showing 9 major climate zones of the European Union. The climatic zone map was based on maps of long-term averages of annual precipitation and temperature, which were constructed using data from approximately 1500 weather stations

(Vossen and Meyer-Roux, 1995). The definition of the climatic zones follows the definition of FOCUS (2000).

The maps were digitally available and were converted to raster maps with a resolution of 10×10 km^2 before the actual overlay was done. As discussed earlier, the leaching assessment should apply to agricultural areas only. Therefore, the overlay was masked with a map showing agricultural land-use (Mücher et al., 1998). The final result was a map with 1442 relevant unique combinations of soil type and climatic zone. The size of the units was between 100 km^2 and 19,600 km^2; the average plot size was 1037 km^2 (Figure 8-2).
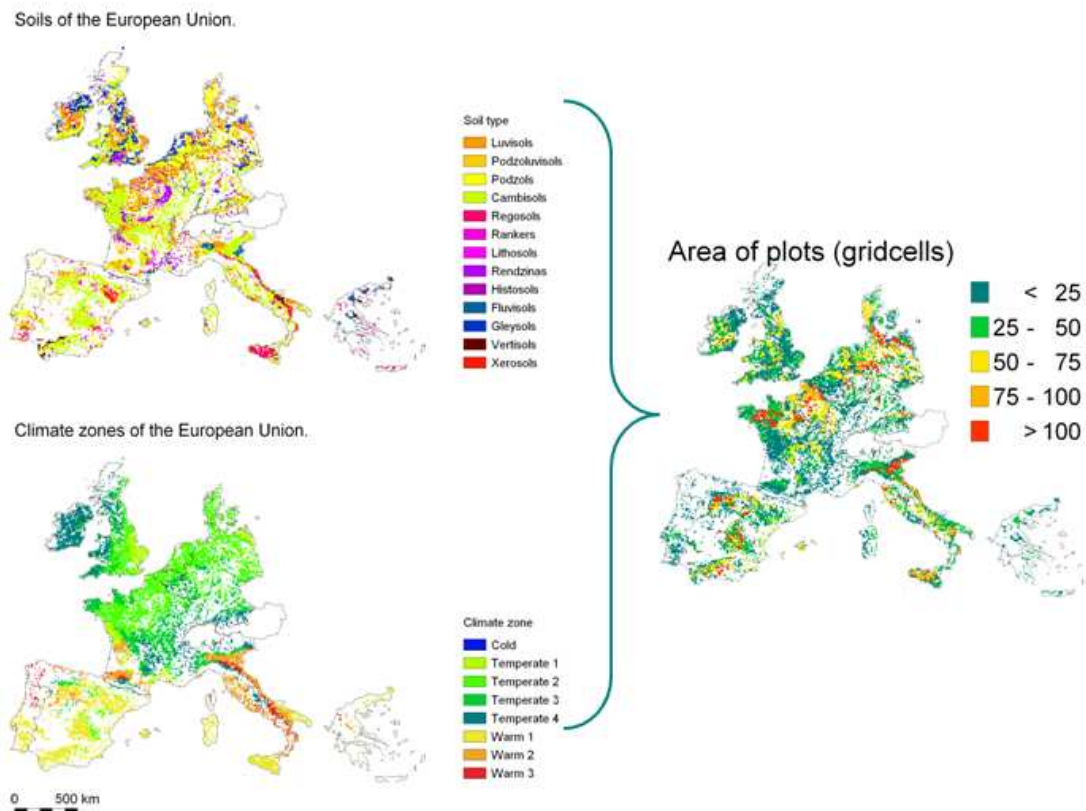
Figure 8-2. Basic maps for EuroPEARL (left) and area of the individual unique combinations (right).

Notice that the spatial schematisation for EuroPEARL was constructed with only 9 climatic classes. This was, however, not the final resolution for the climatic data, because during the parameterisation phase, more detailed climatic information was assigned to each individual unique combination (see Section 8.2.2.4.1).

8.2.2.4 Model parameterisation

During the model parameterisation phase, the unique combinations must be assigned parameter values. Each unique combination can be seen as a higher tier scenario (Section 7.2.5), for which the leaching is calculated with a standard FOCUS leaching model (PEARL, PRZM-3 or PELMO). The reader is therefore referred to the user manual of the individual models. The latest versions of these models and parameterisation documents are accessible through the FOCUS website.

All FOCUS leaching models contain a large number of model inputs. To avoid data redundancy and to assure that the data can be managed in an easy way, we recommend organising the data in a relational data base. As an example, we show the data base that was developed for the EuroPEARL model (Figure 8-3). This database has a hierarchy. At the highest level, a distinction can be made between spatially constant and spatially distributed parameters. Within the EuroPEARL context, simulations were carried out for one single pesticide and one single crop (in other words: a single crop, for example maize, was assumed to be grown throughout the entire intended use area). The substance and crop code were therefore stored at the highest hierarchical level. The 'plot' (or unique combination) is the central entry for all spatially distributed model inputs. As shown in Figure 8-3, a plot was created by overlaying a soil map and a climatic map. The data base structure depends on how the unique combinations are defined. In our example, the third hierarchical level consists of the climatic zone and the soil profile. All other properties are linked to these two entities. Notice that in the EuroPEARL database, crop properties like emergence data and harvest date are related to climatic zones.

8.2.2.4.1 Meteorological time-series

A meteorological time series should be attached to each individual unique combination. Each meteorological time-series must have a length of 66-years and must be created according to the rules given in FOCUS (2000). The MARS database, which gives data at a resolution of 50x50 km^2, could be used for this purpose, but national databases are preferred if available at sufficient resolution. The storage of all meteorological data takes a lot of disk space, particularly if the number of unique combinations is large. Although disk space is not a problem as such, it makes the model less easy to transfer to other people. For this reason, one time-series per climatic zone in combination with a simple scaling procedure could be used to calculate the time-series for each unique combination. This scaling procedure uses the long-term average annual precipitation and temperature (which can be inferred for example from the MARS grid):

$$P_{d,plot} = P_{d,station} \frac{P_{a,plot}}{P_{a,station}} \qquad \text{and} \qquad T_{d,plot} = T_{d,station} + T_{a,plot} - T_{a,station} \qquad (8\text{-}1)$$

where *P* is precipitation, *T* is temperature, and the suffixes *a* and *d* refer to daily and annual, respectively. The central assumption in this approach is that data from one location can be used to correctly describe the seasonal dynamics of weather conditions within the entire climatic zone.
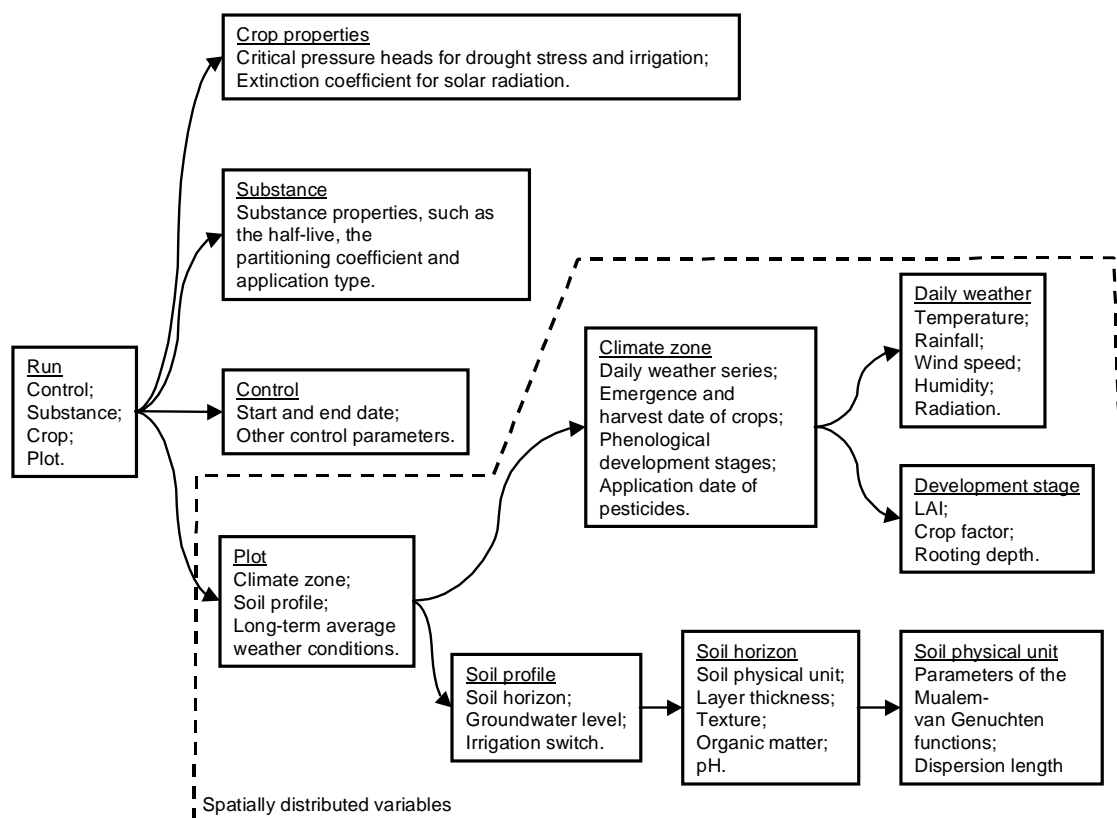
Figure 8-3. Structure of the EuroPEARL data base (source: Tiktak et al., 2004a)

The MARS climatic database contains all parameters that are required for simulation runs with current FOCUS models such as minimum and maximum temperature, rainfall, reference evapotranspiration, and global radiation. The MARS climatic database can therefore be used to extract the daily weather data for European leaching assessments. The MARS database contains weather data spatially interpolated on 50x50 km^2 grids. The original weather observations dataset originate from 1500 meteorological stations across Europe, and are based on daily data from the period 1971 to date. It was compiled from data purchased from various national meteorological services. Some of the data were obtained from the national

meteorological services under special copyright and agreements for MARS internal use only, so that data at station level are not available, only interpolated daily meteorological data are available.

The use of data from local weather stations may be considered if sufficient weather data is available. In GeoPEARL for the Netherlands, for example, data from the Royal Netherlands Meteorological Institute was used. In countries with large altitude differences, the link between station data and unique combinations may not be an easy task. The variability in climatic conditions may be large across short differences. These differences must be taken into account when developing an appropriate geostatistical interpolation technique.

8.2.2.4.2 Cropping parameters

If leaching assessments are carried out across different climatic zones, then dynamic crop properties (crop development stage, harvest date, and emergence date) should be related to climatic zones (Figure 8-3). GeoPEARL has an option to make the crop development dependent on the temperature sum since emergence, which should be used if leaching assessments are carried out across different climatic zones.

Most crop parameters (e.g. date of emergence, date of harvest, crop development stages, etc.) can be taken from the Tier 1 scenario of the corresponding FOCUS climatic zone. See FOCUS (2000) and Chapter 13 for a definition of these climatic zones. In some cases more detailed information on cropping dates exist, in particular when crops are grown in confined areas with characteristic climate conditions. In such cases modifying cropping dates or other parameters may be appropriate. When changing cropping parameters, a rationale for each change must be provided in order to ensure a high degree of transparency in the assessment. If scenarios are developed for minor crops, then a completely new cropping parameterization may be required.

8.2.2.4.3 Irrigation

Siebert and Döll (2001) presented a map showing the fraction of land equipped for irrigation. This map may be used to identify areas where irrigation is a common practice. In those areas and for certain crops, irrigation amounts must be assigned. A procedure that considers the water storage capacity of soils should be used. If the water capacity is not considered, calculated irrigation amounts might be higher than those applied in reality, resulting in unrealistic run-off amounts. Most FOCUS leaching models have multiple options to calculate irrigation amounts – see the manuals of the corresponding models for further information (parameterisation procedures for the scenarios are discussed in Section 11.5.3.

8.2.2.4.4 Lower boundary conditions and runoff

The Darcy-type of models (PEARL and MACRO) needs information about the lower boundary condition (for example depth to ground water). If information on the local ground water regime is available, this information can be used to parameterize the lower boundary condition. PEARL has several options for the lower boundary condition – which of these options is most appropriate depends on the available data. Refer to the GeoPEARL and PEARL manuals for further detail. The lower boundary condition of GeoPEARL for the Netherlands was parameterised through a link between a regional ground water flow model, a simplified surface water concept and the soil water flow model (Wolf et al., 2003; Tiktak et al., 2002). This approach made possible distinguishing between the pesticide flux that reaches the deep ground water and the pesticide flux that reaches the surface water (through lateral drainage). Such detailed information, however, is usually not available for large scale pesticide leaching assessments.

In those cases where no information on the ground water level is available, the ground water depth should be set well below the target depth of 1 m. Tiktak et al. (2004a), used a depth of 2 m depth for their pan-European leaching assessments. They found that the predicted concentration at 1 m depth was hardly affected by the lower boundary condition if the ground water depth is situated well below the target depth.

If runoff is an important process in the area to be simulated, runoff should be simulated as well. See Section 7.2.5.1.4 for details on runoff parameterization.

8.2.2.4.5 Soil parameters

The parameterisation of the soil parameters consists of three steps: (a) selection of a soil profile from a soil profile data base, (b) parameterisation of basic soil information, which is directly available in these data bases (usually horizon designations, organic matter, texture and sometimes also pH), and (c) parameterisation of derived soil properties that are not available in the soil profile database (soil hydraulic functions, bulk density of the soil, etc.).

8.2.2.4.5.1 Selection of a soil profile

Soil profile descriptions usually contain information on the soil mapping unit from which the soil profile originates. The link between the soil map and the soil profile data base is then a trivial step, because there is a 1:1 link.

At the European level, however, this link is not straightforward. The problem is that the Soil Mapping Units (SMU's) at the EU-soil map are association of dominant and subdominant Soil

Typological Units (STU's). The STU's and not the SMU's are the carriers of basic soil information, such as the FAO soil name and the soil textural class. For this reason, the link between the soil map and the profile data base needs to be done in two steps. A possible approach could be to determine the dominant STU, and then assign a soil profile to this dominant STU. Notice that during this step information on subdominant soil profiles will be lost, leading to a possible bias during the assessment (Vanclooster et al., 2003). An additional problem is that the Soil Profile Analytical Database of Europe (SPADE, Madsen-Breuning and Jones, 1995) usually does not contain explicit information on the associated soil typological unit. Finally, many STU's at the EU-soil map do not have an associated soil profile. To overcome these problems, Tiktak et al. (2004a) developed a two-step approach for the parameterization of EuroPEARL (Figure 8-4). In a first step, the dominant STU within each SMU was determined. Then, a soil profile was assigned to the dominant STU. This second link was made at different confidence levels. The most reliable link could be obtained if the author of a profile has explicitly stated the corresponding STU. If the STU was not specified, a profile was assigned on the basis of the full FAO soil name, the textural class and the country code. By including the country code in the query, soil profiles from the soil profile data base of a given country could only be matched to Soil Mapping Units within that country. In those situations where assigning a soil profile was still not possible, the query was repeated with the full FAO soil name and the country code only. Finally, a query was carried out using the major soil type only (e.g. Cambisol instead of Eutric Cambisol). Using this procedure, 1062 Unique Combinations could be assigned a soil profile, representing approximately 75% of the total agricultural area of the European Union. Unfortunately, Austria, Sweden and Finland had to be left-out, because there was insufficient soil profile information available for these countries.

SMU
SMU number;
Country;
STU 1 number;
STU 1 coverage;
....
STU n number;
STU n coverage;

Dominant STU number[1]

1

STU number[1,2]
Country[2];
FAO Soil Name[2];
Texture class[2];
Other parameters.

2

Soil Map of Europe

Soil Profile Analytical Database

Soil profile number
(STU number)[2];
Country[2];
FAO Soil Name[2];
Texture class[2];
Horizon numbers[3];
Other parameters

3

Soil Horizon number[3]
Horizon depth;
Profile number;
Organic matter;
Texture;
pH.

Figure 8-4. Link between the EU-soil map and SPADE-1. Parameters with suffix 1 have been used for the link between the SMU and the STU; parameters with suffix 2 have been used for the link between the STU and the soil profile number, and parameters with suffix 3 have been used for the link with the soil horizon tables.

8.2.2.4.5.2 *Parameterization of basic soil data*

If a national soil profile data base is available with sufficient quality, then this data base should be used to support national registration procedures. These data bases usually have a higher resolution and are often of better quality than the pan-European data bases (which are estimated soil profiles). Also, these data bases usually reflect local conditions better than pan-European databases.

If such soil data is not available, the Soil Profile Analytical Database of Europe could be used. Please refer to section 7.2.5.2.4.6 (step B) for procedures.

8.2.2.4.5.3 *Parameterization of derived soil data using pedotransfer rules*

Bulk density and hydraulic properties are usually not available in soil profile databases. These parameters must therefore be derived by so-called pedotransfer functions. See Section 7.2.5.2.4.6 (step C) for details.

In some countries, pedotransfer functions are available which are based on local or national soil inventories (for example the Staring Series by Wösten et al., 1994). If such pedotransfer

function are available, their use is recommended because they reflect local soil conditions better than general purpose pedotransfer functions like HYPRES and Rosetta.

8.2.2.4.6 Pesticide properties and application scheme

The user has to specify pesticide properties and application schedules. Because the core of the spatially distributed model is a normal FOCUS leaching model, the reader is referred to the manuals of these models. Because spatially distributed leaching assessments are Tier 3 assessments, the user may want to use the parameter refinements that have been developed for Tier 2 assessments. However, these refinements should be shown to be applicable for the intended use area (through for example extrapolation or scaling of lysimeter results, see Section 8.3). With respect to pesticide application, the user may want to link the application date to the crop emergence data or another event in the crop development table. This is particularly important if the simulations extend through different climatic zones.

8.2.2.5 Running the FOCUS leaching model and plotting the results in a map

An assessment with a spatially distributed leaching model comes down to running a FOCUS leaching model multiple times (Figure 8-5). A spatially distributed model starts with reading the spatial schematisation, pesticide properties and application schemes. This is done only once (left-hand side of figure). The spatial schematisation procedure results in a file or database table, which contains for each unique combination or plot the basic spatially distributed parameters, such as the soil profile number, the weather district and the crop number (see Figure 8-4). For each individual plot, a single line from this file is read. Using this information, related variables are selected. The soil profile number, for example, is used to select horizon designations and soil properties from the soils table in Figure 8-4. After this selection, pedotransfer functions are applied to calculate derived variables, such as the dry bulk density of the soil. Using all this information, a FOCUS PEARL input file is generated, and the model is executed. The entire procedure is repeated until all relevant unique combinations have been processed.
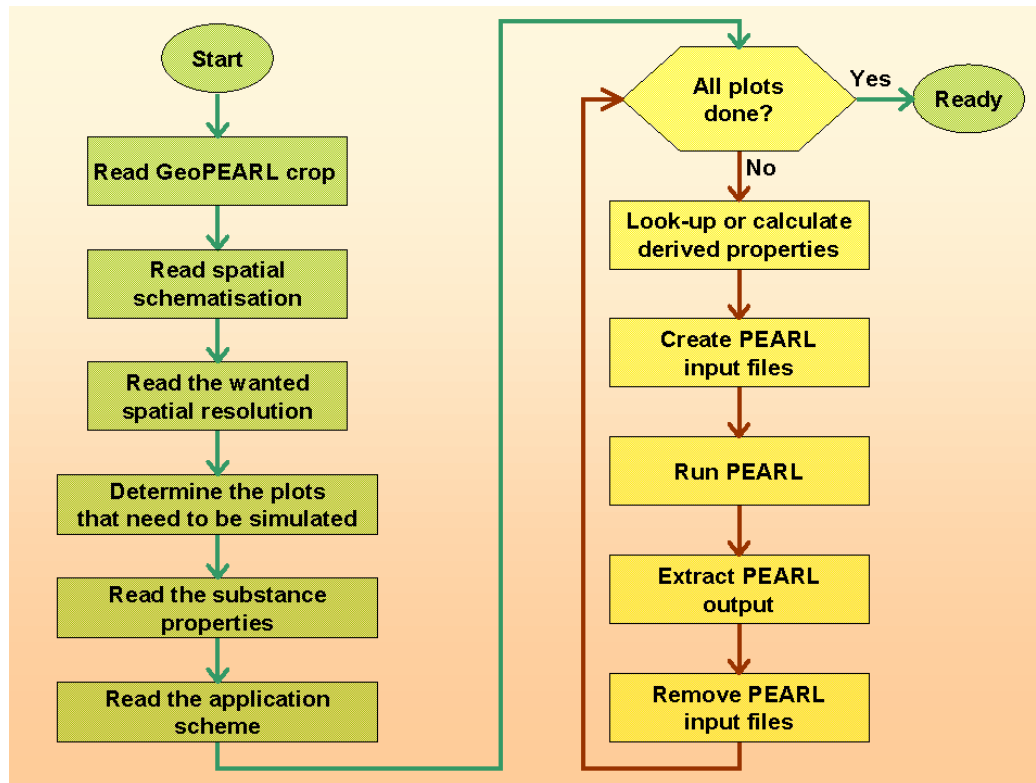
Figure 8-5. Flowchart of the GeoPEARL model (after Tiktak et al., 2003). Actions in green are performed once, actions in yellow are repeated for each unique combination.

The schematisation procedure also resulted in a map showing the position of the unique combinations (here referred to as 'plot map'). Maps of calculated results can be obtained by combining in a Geographical Information System the simulated values with the plot map. In GeoPEARL, this action is performed in the GeoPEARL User Interface, which is available with the model (Tiktak et al., 2004b).

8.2.2.6 Calculation of the target quantity

The target quantity is calculated from the cumulative frequency distribution of the leaching concentration. The target quantity e.g. following the FOCUS methodology could be calculated in two steps:

1. For each unique combination the 80[th] percentile target leaching concentration from a time-series of 20, 40 or 60 years is calculated , using the normal FOCUS procedures (FOCUS, 2000).
2. The target spatial percentile is then derived from the cumulative frequency distribution of the leaching map.

When calculating the cumulative frequency distribution, the spatial distribution of the target crop should be used as a weighing factor. Not considering the intended use area may result in unrealistic frequency distributions as shown in Figure 8-6 for an example at the national level of the Netherlands.
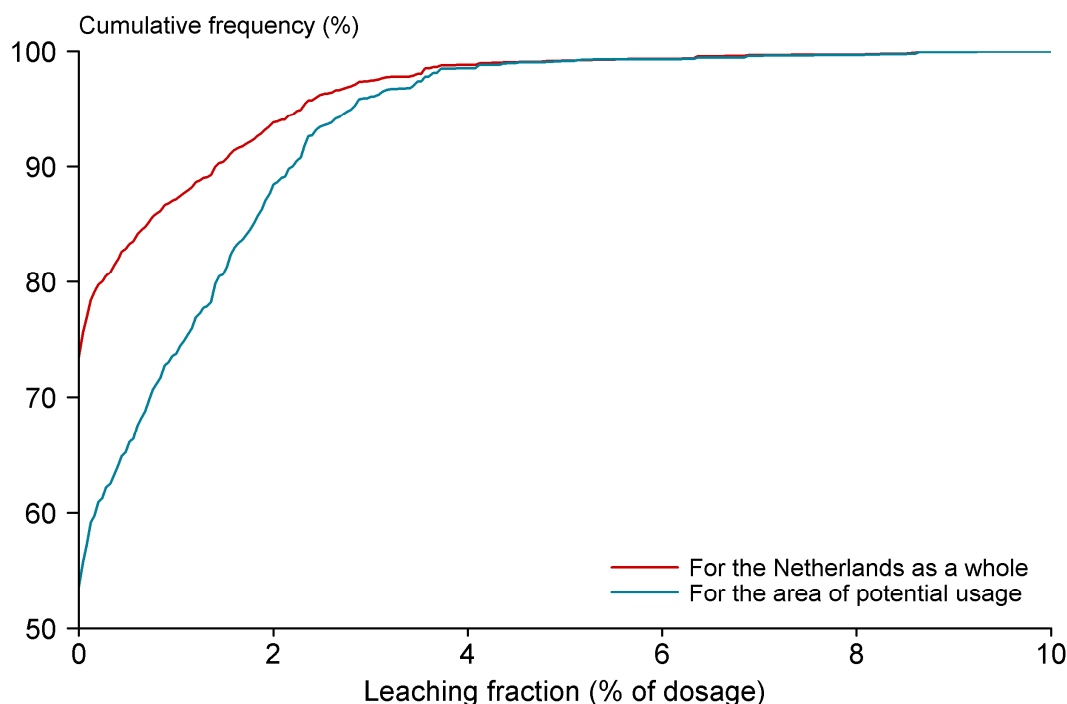
Figure 8-6. **Effect of considering the intended use area on the calculated frequency distribution of the leaching concentration (using the Netherlands as an example for a political entity).**

The spatial distribution of crops can be obtained from maps based on satellite images. These satellite images have an extremely high spatial resolution (up to 25x25 m^2), but the number of crops distinguished is limited (only major crops are mapped). To obtain the spatial distribution of other crops, the satellite images can be combined with census data, which in many countries are available at the level of municipalities. See further Kruijne et al. (2004).

8.2.3   *Stochastic assessments*

The proposed procedure for spatial schematisation relies on the soil map as a carrier of information relevant to solute transport. Indeed, variation between soil types has been shown to be usually larger than within-soil variation (for example Bergström and Jarvis, 1993; Brown et al., 2000). Nevertheless, no soil-classification scheme can fully capture the

complexity of soil variation, and therefore the inherent stochastic variation remaining within each class should be assessed (Jarvis and Dubus, 2006). Leterme et al. (2007b) performed such a probabilistic assessment for atrazine leaching in a Belgian catchment, using Monte Carlo simulations. They showed that the spatial pattern of pesticide leaching was not strongly affected, but the simulated concentrations increased by an order of magnitude when looking at the 80th percentile, as done in current FOCUS procedures. The increase of the 80th percentile was to be expected, as the incorporation of within-soil type variability is likely to introduce more extreme scenarios. Another limitation of deterministic models like GeoPEARL is that pesticide properties are taken spatially constant. In reality, however, these properties exhibit spatial variability (e.g. Walker and Brown, 1983; Charnay et al., 2005). The introduction of spatial variability of pesticide properties in stochastic simulations also increases the leaching concentration, as shown by Leterme et al. (2007b).

Despite the fact that scientists now believe that stochastic assessments should be an integral part of the decision making process (EUFRAM, 2005), the current working group chooses to limit tier 3 simulations to deterministic simulations. One of the reasons is that standardisation procedures for stochastic assessments are currently not available, and that the effect of user subjectivity in performing stochastic assessments is still too large. Leterme et al. (2007b), for example, showed that the effect of truncation of distributions of soil and pesticide properties has a large effect on the predicted leaching percentiles. Also, the outcome of deterministic assessments is in line with the operational definition of the protection goal as given in Section 3.1, although note that the definition of soil mapping units is scale dependent. Further research and progress in the area of stochastic assessment may lead to a revision of the recommendation.

8.3   Higher tier leaching experiments set into context by modelling (Tier 3c)

The broad potential for using higher tier leaching experiments in the assessment of the risk to ground water has been covered in Chapter 4. This current section considers the practical possibilities, limitations and concerns about the use of such studies, and their placement into context by simulation modelling. Note that since these are higher-tier approaches, the lower tiers usually will have indicated potential risks. These assessments (i.e. the studies and the associated modelling) must then deliver sufficient evidence to prove the potential risks are unlikely to exist in reality.

Generally, the appropriate context for the experimental studies can be provided in a so-called "pre-processing" manner (i.e. explicitly designing the experiment with the intent to cover the

location and agroclimatic conditions that address the required protection goal for the particular compound and use). A so-called "post-processing" manner (i.e. the field and lysimeter observations are used to refine model parameters or model calculations) is then required to demonstrate whether the intent of the pre-processing phase was achieved. Pre-processing approaches alone will not lead to the experimental result being directly suitable for regulatory decision-making (e.g. the rainfall at the chosen location over the experimental duration may be significantly less than the target). Poorly designed studies (i.e. of short duration with no understanding of the movement of chemical through the soil profile) cannot necessarily become relevant for regulatory decision-making by post-processing extrapolations. Therefore, while post-processing is essential, a combination of both approaches usually will give the most robust results for regulatory decision-making.

Sections 8.3.1 and 8.3.2 concentrate on the advantages/disadvantages and regulatory status of the experimental studies, followed by Section 8.3.3 on appropriate pre-processing issues to consider. Section 8.3.4 then consider particular post-processing approaches in detail, i.e. scaling of model parameters based on inverse modelling and scaling of the leaching assessments based on observed differences between simulated and observed field/ lysimeter leaching.

8.3.1 Study types and their applicability for different agroclimatic conditions

8.3.1.1 Lysimeters

Regulatory lysimeter studies utilise an undisturbed soil monolith (typically 1 m deep and 1 m^2 surface area) to grow a crop and follow the breakthrough of radiolabelled pesticide and metabolites over time (See Fuhr and Hance, 1992; and Fuhr, 1998 for general reviews). This experimental design confers the advantage that a flux-weighted concentration at 1 m depth can be measured without necessarily completely understanding the mechanistic nature of the actual degradation and sorption processes of the pesticide in this soil.

Due to the inherent experimental design of the lysimeters that were usually used for regulatory submissions (i.e., this is not a function of particular study guidelines), the water flow at the bottom boundary does not exactly replicate the real field situation, being free draining rather than hydraulically connected to deeper soil depths. This is acknowledged as a potential weakness in the design but is unavoidable if the flux-weighted annual concentration of pesticide is to be obtained as the endpoint. Early assessments by Hance and Fuhr (1992) have suggested that lysimeter and field studies result in similar amounts of pesticide remaining in the soil profile. Studies by Jene (1998) concluded that free-draining

sandy soil lysimeters (0.8 m^2 surface area) and suction cup instrumented field plots (2.7 m^2 surface area) of the same soil type showed no system-related differences in water and solute (including pesticide) transport. Although (i) the outflow water volumes of the field were about 60% of those in the lysimeter and (ii) the average flux concentration of benazolin in the field was about two times higher than in the lysimeter, the sites were 20 km apart so differing evapotranspiration (ET) amounts at the two locations were considered by Jene (1998) to account for the difference. Extensive studies in a very similar experimental set-up, but with the lysimeters placed at the field site (both being silty soils), showed water percolation in the field trial (water collected via suction plates) was 67% of that in the lysimeter study. Comparisons of the leaching of two pesticides (ethidimuron and methabenzthiazuron) give 3.3 and 0.7 µg/L annual average leachate concentrations of ethidimuron in the lysimeter and field, respectively, and 2.8 and 0.05 µg/L annual average leachate concentrations of methabenzthiazuron in the lysimeter and field respectively (but with large variations amongst replicates). In both systems this leaching was considered to be the result of preferential flow (Dressel, 2003). Further analysis of these results by Kasteel et al (2007) suggested that methodological issues regarding the suction plates could have led to underestimation of the water flux. The mass recovery of bromide tracer was identical despite these water volume differences but the spreading (dispersivity) was stated to be greater in the lysimeters, leading to lower peak concentrations. Subsequently the authors attempted to simulate the field results to account for the effect of the suction plate and concluded that the "true" dispersivities were similar in the field and lysimeter. (note that for non-conserved solute this behaviour would be likely to lead to higher concentrations leached due to more compound moving out of the zone of optimum degradation). The complexities of the experimental system mean that broad conclusions about comparative amounts of leachate from lysimeters and field systems should not be drawn from this single experiment.

Computer simulations (Boesten, 2007) have indicated that predicted pesticide concentrations were always lower with the lysimeter bottom boundary type than with the field bottom boundary type (hydraulically connected to ground water).

Significant infrastructure is required to maintain lysimeter cores during an experiment and hence the cores can only be subjected to a limited range of meteorological conditions (i.e. particular locations in northern Europe that have lysimeter facilities). There are also agronomic restrictions due the relatively small surface area of the lysimeter. Therefore experiments with tree and other permanent crops are often impractical and ridged cropping systems (e.g. potatoes) may be difficult to maintain.

The use of tracers in lysimeters is a useful approach and should be considered in future to determine the hydraulic properties of the soil cores.

Research lysimeter facilities may additionally include packed cores, longer lysimeter cores (>> 1m) with increased residence times, or devices to apply suction to the bottom of the lysimeter core to overcome the capillary fringe. They are often used to follow water or solute movement. Further current information on these can be found on the internet at the following website: www.lysimeter.com

8.3.1.2 Field leaching experiments

Field leaching experiments have the advantage that they are undertaken in actual agronomic situations (i.e. any field) and require no particular facilities. Therefore they can be used in a wider range of climatic situations and locations than typically occur for lysimeter studies (e.g. also in southern Europe). Leaching can be assessed for agricultural practices that are impractical for lysimeters e.g. ridged systems for potatoes, permanent crops etc. However a disadvantage is that radiolabelled compounds cannot be used so compounds of interest must be determined prior to the study (and analytical methods be available) and mass balances cannot be obtained. Water is drawn out of the soil profile or taken directly from ground water at different depths and analysed for the presence of the compounds of interest. Therefore the annual average concentration cannot be directly determined, only the concentration at a given depth at a particular time. Water balances are also not directly obtained, although approximations of the ground water recharge can be used to estimate an annual average from these data. In addition there can be methodological issues about the method by which the water is drawn out of the soil profile (e.g. using suction cups, see Carter and Fogg, 1995; Weihermüller et al, 2005, 2006; and Ferrari et al, 2007, for discussion on appropriate methodologies). Using 'equilibrium tension plate lysimeters' [11], drainage rates and leaching concentrations can be measured continuously and more accurately. These systems consist of large ceramic plates which are connected to a vacuum to apply suction to the soil water. In order to minimize the disturbance of the water flow by the suction plates, the applied suction is controlled so that tensiometer measurements in the soil just above the suction plate match with tensiometer measurements at the same depth in the soil profile where water flow is not influenced by the suction plates (Byre et al., 1999; Kosugi and Katsuyama, 2004; Mertens et al., 2005).

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[11] Note that the name implies that this methodology could also be a "lysimeter" study. Nonetheless it has been designated as a field leaching study in this document because it has more in common with field leaching type approaches than with the standard regulatory type "lysimeter" study.

Regarding regulatory use of field leaching study, the same principles apply as for lysimeter studies. Therefore, a field leaching study would need to be set into context by modelling before it can be used for regulatory decision making.

Further useful information on leaching potential may be obtained from analysis of soil cores at differing depths. Note that certain leaching study designs could be considered very similar to monitoring studies (for which guidance is provided in Chapter 9).

8.3.2 Current status of higher tier leaching experiments in national regulation and appropriate guidelines

Within the EU there is national guidance for undertaking lysimeter studies in Germany (BBA, 1990) and in the Netherlands (CTB, 1999). In Germany, if the conditions of the guideline are met, the results are considered directly acceptable for national regulatory decision-making. A recent comparison of BBA guideline-compliant experimental data and national scenario simulation studies (see Figure 8-7) suggested a high degree of agreement between the two approaches in evaluating whether the regulatory endpoint of 0.1 µg/L is exceeded. This figure effectively demonstrates the consistency of the German national tiered approach as outlined by Michalski et al. (2004) and highlights the infrequency of disagreement between lysimeter and simulation results.
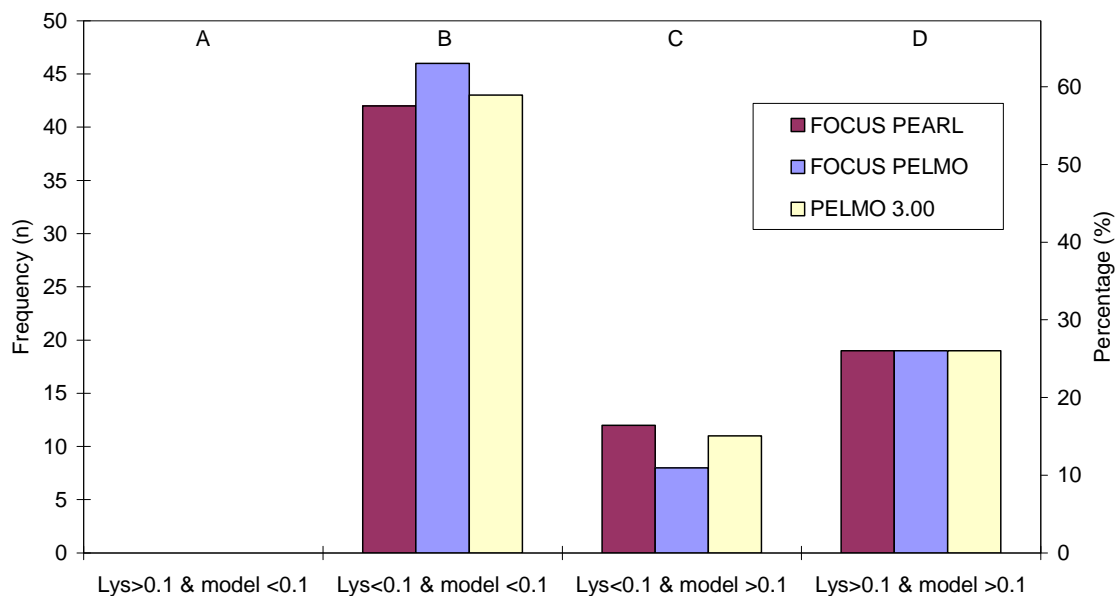
(Modelling was performed using the standard Tier 1 scenarios (no re-modelling of the lysimeter study scenario with special parameters; PELMO 3.0: Borstel soil & Hamburg weather scenario as per current UBA guidance FOCUS PELMO: only the Hamburg scenario)

Figure 8-7. Comparison of lysimeter results and model calculations for the Hamburg scenario (Hardy et al, 2008)

In the Netherlands, an additional normalisation process is frequently required for data from lysimeter studies (Verschoor et al., 2001; see also Section 8.3.4.2). As part of this, a comparison to the simulation results using the best case DegT50 (shortest) and K_{oc} (highest) values from the regulatory data package may be undertaken (in the absence of soil-specific DegT50 and K_{oc} values for the lysimeter soil) to demonstrate that even values at the most favourable extreme of the available data would have been expected to result in simulations of >0.1 µg/L. Hence, experimental results of <0.1 µg/L would be unlikely to have resulted simply from the choice of favourable soil conditions for compound degradation and sorption. Other guidelines for lysimeter studies are also available (OECD, 2000; MATS guideline; NACA, 1994), but these are not directly incorporated into national regulatory schemes.

The work group is unaware of any specific recognised regulatory guidelines for field leaching experiments under EU conditions. However, guidance from the CTB (Cornelese et al., 2003) provides information on monitoring in the upper ground water (< ca 5m depth) which can be considered as a form of field leaching since the link between pesticide application and concentration in the upper ground water is specifically stated (see Chapter 9 for relationships

between monitoring and field leaching studies). The broad requirements for this type of study are stated to be: 8-10 fields with 12-20 sample locations/field and 3 time points (before, during and after the simulated peak concentration). Guidance similarly exists for prospective ground water studies conducted in the U.S. (US EPA, 1998), which are also considered as a variation of a field leaching study. A possible outline protocol for a regulatory field leaching experiment is currently in preparation in Italy (Ferrari et al., 2007), although note that this is only directed at studies abstracting shallow ground water (and not soil pore water).

8.3.3 Suitability for exposure assessment within FOCUS framework – "pre-processing" aspects

The critical point in the use of higher tier leaching studies (both lysimeter and field leaching) in the FOCUS framework is the demonstration of adequate vulnerability. The Tier 1 simulation scenarios have been developed with the intention that they cover the 90[th] percentile overall vulnerability. For experimental field data to fit logically into the FOCUS framework they must cover a similar vulnerability. This section concentrates on addressing vulnerability via "pre-processing" approaches. As noted elsewhere "post-processing" approaches to putting the experimental data into context may allow greater flexibility in the nature of the initial experimental data.

This question of study vulnerability can be separated into two main components;

1. Is the inherent study design sufficiently conservative to address the leaching process?

2. Is the experiment located in a sufficiently vulnerable location with regard to soil type, agronomy and meteorological conditions?

8.3.3.1 Determining adequate vulnerability – through study design

8.3.3.1.1 Lysimeters

The most often raised concerns regarding lysimeter studies relate to the translation of the concept into recognised methodologies that are applicable for regulatory decision-making, primarily BBA guideline 4-3 (BBA, 1990); since other guidelines are largely derivative of this. Typically the experiment is undertaken for a period of three years only (with a second application in the second year), uses a sandy soil type only, and has very limited replication (typically two cores but even one core is conceivable, although this does not comply with the OECD guideline). These limitations are all valid scientific concerns and are considered individually in the following sections.

Within the FOCUS framework, lysimeter (and field leaching) studies are clearly a higher tier within the decision-making scheme, so logically such studies are likely to be triggered for

fewer compounds. Possibly such compounds will be those with different behaviour as defined in Section 11.1. In such cases the use of a "standard" guideline (e.g. BBA guideline 4-3) may not be appropriate (for pre-processing approaches) and a greater emphasis on compound-specific study design should be considered.

8.3.3.1.1.1 Soil type

The standard BBA regulatory guideline study requires a sandy soil of low organic carbon content (<1.5%) since this is generally considered to be the worst case for chromatographic flow movement of a pesticide. Evidence to support this view comes from a study (Gottesbüren, personal communication, 2008) in which the leaching of bromide has been measured in parallel running lysimeters with two different soil types (sand and loam). Results are shown in Figure 8-8. Bromide breakthrough started earlier and reached higher cumulative outflow in the sandy soils, whereas in the loamy soils the cumulative breakthrough was considerably lower and reached a maximum range of 4 – 14 % of the applied dose by the end of the study. Gottesbüren (personal communication, 2008) attributes the removal of the remaining bromide from the soil to plant uptake. The faster chromatographic flow processes in the sandy soils observed for bromide in this study would also have more quickly transported potentially leaching pesticides into deeper soil zones, in which the degradation rate would be lower.
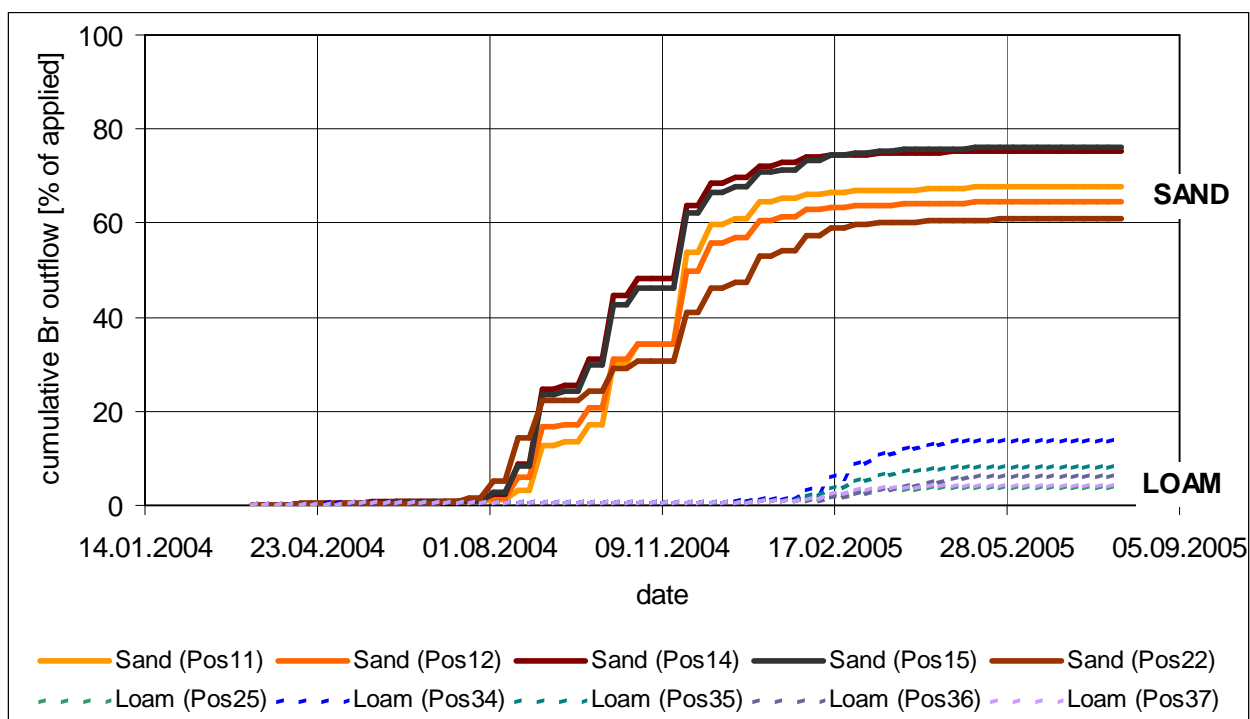
Figure 8-8. Bromide breakthrough in replicate sand and loam lysimeters running in parallel at the same facility (Gottesbüren, personal communication, 2008).

pH characteristics are not specified in the BBA guideline and, in practice, the pH will vary depending on liming before the cores were taken or the study started. pH characteristics can influence both the sorption and degradation of a pesticide and its metabolites and so a worst case situation could only be considered on a case by case basis.

Whether for most pesticides these conditions of acidic pH and sandy soil, which prevail in most regulatory lysimeter studies, will also be the worst case for degradation is uncertain. That low organic carbon contents lead to reduced microbial activity and slower biological degradation rates for pesticides is widely believed, although there appear to be no data reviews to demonstrate that this belief is defensible. In fact an earlier review (Walker and Allen, 1984) suggested that degradation was faster in sandy soils than more clayey soils for the herbicides simazine and metamitron. However, the same review points out that other factors also influenced degradation rates and that overall the difference in degradation rate among a number of soils with differing characteristics was relatively small.

Overall the worst case for leaching will be a combination of the factors discussed above. Therefore consideration of the actual amounts leached from various soil types under identical

meteorological conditions is a strong indicator of the overall vulnerability of the particular soil to the particular pesticide and/or its metabolites. Table 8-1 shows some published comparisons where leaching from the gleyic cambisol (sandy) was greater than that from the orthic luvisol soil (silty loam). However, note that the results refer to total radioactivity in the leachate and hence would include more hydrophilic metabolites, CO_2 etc.

Table 8-1. Selected Lysimeter Studies with Different Soil Types Performed at the Institute of Radioagronomy (Führ et al., 1998)

Compound	1st crop	Period	Soil Type	%AR in leachate
Atrazine	Maize	05/1989 – 06/1991	Orthic Luvisol (OL) Gleyic Cambisol (GC)	2.0 2.0
Chloridazon	Sugar beet	04/1989 – 05/1991	OL GC	0.3 7.1
CL 23601	Maize	07/1991 – 07/1991 ??	OL GC	< 0.1 0.2
Clopyralid	Sugar beet Sugar beet Oil seed rape	06/1988 – 08/1990 06/1989 – 07/1991 02/1992 – 03/1994	OL GC GC	0.6 0.4 0.5
Dichlorprop-P	Summer barley	05/1989 – 06/1991	OL GC	0.1 0.3
Pyridate	Maize	05/1989 – 06/1991	OL GC	0.1 0.3
Quinmerac	Summer wheat Sugar beet	05/1988 - 04/1990 05/1990 – 05/1992	OL GC	0.8 3.7
Terbuthlyazine	Maize	05/1989 – 05/1991	OL GC	3.2 10.4

In contrast, other lysimeter studies (Brown et al., 2000; Yon, 1992; Bergstrom, 1994) have determined greater pesticide losses in non-sandy compared to sandy soils. By-pass or macropore flow was stated to be the reason for the leaching from heavier soils in at least some of these cases.

As stated previously, the assumption that sandy acidic soils will ultimately result in the worst case leaching conditions for all pesticides is simplistic. However, leaching assessments at the EU level (though not always those at national levels) are currently based on the premise of chromatographic flow only (and the dispersion length used in simulation models is set independent of soil type). Therefore, at this time, consistency with the existing EU Tier 1, implies that further assessment of the influence of soil type on pesticide leaching should be confined to the aspects relating to chemical-specific interactions (e.g. sorption, degradation)

and not macroporous flow. Data on degradation and sorption of the parent compound in at least four soils (at least three soils for metabolites) is available from the standard regulatory package and this can be examined to assess influences of soil type on sorption and degradation. This is a relatively small data-set on which to assess particular influences of soil characteristics and subtle effects would be difficult to observe. However, this data set is the same that is used for the Tier 1 input parameters and seems a reasonable basis on which to investigate whether the assumptions incorporated into the simulations at Tier 1, hold true for the same soil types under outdoor conditions at Tier 2. In the absence of any clear effects of soil type on compound behaviour, the current BBA guideline standard soil type (low organic carbon, sandy soil), which is highly likely to be a worst case with respect to the sorption coefficient, can be used for lysimeter studies as a default. However, a more detailed consideration of the potential usage area to determine an 80^{th} percentile worst case soil (see Section 8.3.3.2) would be preferable.

8.3.3.1.1.2 Duration

The duration of all regulatory lysimeter experiments is significantly shorter than would be necessary for maximum compound breakthrough of most compounds according to simulation studies (Boesten, 2007). The requirement for the duration of lysimeter experiments is assumed to be a pragmatic decision to enable data to be collected over a realistic timescale for regulatory use, but no documented information has been found on this point. Some data collected from regulatory studies has suggested that over the standard three year duration of the BBA guideline study (Hardy et al. 2008) peak concentrations were obtained during the study. In 34 lysimeter studies with the total sum of 63 substances the maximum annual average concentrations (AA) were mostly reached in year 1 or in year 2 of the study (Table 8-2). The duration of the majority of the 34 studies was 3 years (N= 21; 62%), whereas 11 studies lasted 2 years (32 %), in 1 study the duration was 4 years and in 1 study only 1 year[12].

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[12] The development of the compound in this study (7) was stopped after the 1st year due to unacceptable leaching

Table 8-2. Year of maximum annual average leached concentration in the lysimeter.

Study	Spring / Autumn	Rate (g/ha)	No. years	Year of max Annual Average			
				Parent	Met 1	Met 2	Met 3
1	S	70+40	3	< LOD	1		
2	S	125+75	3	1	1	2	
3	S	1440	3	<LOD	2	2	
4	S	750	3	2			
5	S	750	2	1			
6	S	500	3	2			
7	S	375	1	1			
8	S	2600	2	1			
9	S	25	3	1 or 2			
10	A	250	2	1			
11	S	25	3	<LOD	<LOD		
12	A	60	2	<LOD			
13	S	500	2	<LOD			
14	S	70+70	3	1	2		
15	A	200+200	3	<LOD	3		
16	S	400+400	3	<LOD	<LOD		
17	S	500+500	3	1	1	1	
18	S	15+15	3	<LOD			
19	A	15+15	3	<LOD			
20	S	15+15	3	<LOD	1		
21	S	200+300	4	<LOD			
22	S	1000	2	<LOD	1	<LOD	<LOD
23	A	1500	3	<LOD			
24	S	1500	3	<LOD			
25	A	1500	2	<LOD	1	1	
26	S	1250	3	1	1&2	1&2	
27	A+S	50+60	3	1&2	2&3	2	2&3
28	A+S	60+50	3	<LOD	1	1&2	
29	S	900	3	<LOD	2&3	1-3	1&2
30	S	7.5+7.5	3	1-3	1-3		
31	S	30+30	3	<LOD	<LOD	<LOD	
33	S	200+200	2	1&2	1	1	
34	S	200+160	3	1&2	2	2	

In less than 5 % of the cases (3 of 63 substances (all were metabolites)) the highest annual average leachate concentration occurred in the last year of the lysimeter experiment.

The median annual leachate volume measured in the 34 lysimeter studies were shown to be 308 mm (Hardy et al., 2008). A considerable fraction (median: 36%) of the precipitation and irrigation percolates through the lysimeter cores.

This provides some support for the duration of lysimeter studies according to the BBA guideline. However, the strength of the evidence provided by this table is conditional upon the behaviour being totally chromatographic in all cases (i.e. no subsequent annual increase in compound leaching after an annual decline). Note that work by Dressel (2003) concluded that loses of methabenzthiazuron and ethidimuron from lysimeters with an orthic luvisol were by preferential flow mechanisms.

Broadly speaking the void volume of a 1 m depth soil core is approximately 250 mm (approximately 1 year of recharge for BBA guideline conditions – although a particular minimum recharge is not a requirement of this guideline). A more detailed examination of the expected breakthrough of the target compound (parent or metabolite) at the bottom of the lysimeter should be provided as part of the study design for both lysimeter and field leaching experiments and studies should be continued at least until this time is reached. This is likely to increase the timescale of the study in comparison to existing guidelines but, for pragmatic reasons, five years may be the realistic limit of regulatory usefulness. In addition destructive sampling of the core at the conclusion of the experiment as required by the BBA (BBA, 1990) and OECD (OECD, 2000) guidelines should be undertaken to obtain more information on compounds still in the core (this may also be particularly helpful if inverse modelling is used as a post-processing approach). Application should occur in each year, unless there are particularly strong reasons from the GAP that this is not appropriate (in which case a further justification on why the results can be considered to demonstrate appropriate vulnerability, would be required). In addition, the recharge in each year should be typical of the conditions that are being investigated (i.e. for 800 mm rainfall under BBA lysimeter guidelines, the recharge should be about 250 mm rather than, for example, 80 mm).

8.3.3.1.1.3 Replication

Replication is a significant issue, which was discussed as far back as 1992 (Fuhr and Hance, 1992). It is always of greater importance in field experiments where there are a larger number of variables and uncertainties compared to laboratory studies. For undisturbed soil monoliths 1 m^2 is a relatively small surface area and hence even the variation of soil hydraulic properties over a field are unlikely to be fully reflected in the sample size (soil heterogeneity is also an aspect to be considered for laboratory studies but in these cases at least maintenance of soil structure is not necessary).

Given the variability of leachate results between cores in lysimeters (see for example, Jene, 1998), a single replicate is clearly insufficient to obtain scientifically valid results. On the other hand too large a number of cores would make the studies prohibitively expensive. The use of triplicate soil cores for lysimeter studies would seem to be a reasonable compromise.

8.3.3.1.1.4 Scale and uncertainty

In absolute terms the uncertainty (this is defined as the uncertainty of the result covering the 90[th] percentile worst case, or equivalent regulatory endpoint, and will account for the variability in the individual factors that contribute to the overall leaching) surrounding the result of a lysimeter experiment is very difficult to quantify since multiple data sets covering many different cores and soil types are not realistically available. The variability can be sub-divided into a number of possible factors (e.g. possible variation in DegT50 in soil, Kd etc.), but precisely how these interact to give the range of the experimental endpoint is never certain. In addition to inter-field variation in the degradation rate and sorption of pesticides, intra-field variation is also well-known (e.g. Beck et al., 1996; Walker et al., 2002; Rasmussen et al., 2005). This has often been attributed to differing population of micro-organisms in different parts of the field (e.g. Rasmussen et al., 2005; Walker et al., 2002) and variations of DegT50 within a field have been stated as 6.5-30 days (Walker et al., 2002) and 31-483 days (Beck et al., 1996).

Attempting to consider these aspects relative to the uncertainties and variability in the Tier 1 data is perhaps simpler, although this also brings some difficulties as the sources of the uncertainty are not directly comparable. In a tiered assessment scheme, higher tiers should provide equal or greater re-assurance on these aspects than the lower tiers. Standard laboratory degradation and sorption studies generally use very small soil masses (typically 50-100 g) in duplicate samples. However, four contrasting soil types (from widely differing fields) are investigated in regulatory submissions (whether each soil is systematically sampled to fully account for intra-field variation is not certain). Lysimeter experiments typically investigate only one soil type but use a much larger mass of topsoil. Therefore based on the relative masses more of the intra-field variability would be expected to be reflected in a field study than a laboratory study. However, when considering current regulatory approaches, more inter-field variability in sorption and degradation parameters is addressed by laboratory studies.

8.3.3.1.2 Field Leaching Studies

As mentioned previously, there are very few recognised guidelines for these studies. In general, when designing a study some of the same factors need to be considered as for the lysimeter study i.e. replication and duration while other factors that need consideration are unique to this study type (e.g. method of water sampling, depth of sampling).

8.3.3.2 Determining adequate vulnerability – through location selection

There are two broadly acceptable approaches to determine adequate vulnerability of the location of lysimeter and field leaching studies (to be undertaken prior to conducting the study):

(1) Conduct a GIS analysis to obtain the intended regulatory vulnerability (90th percentile based on rainfall and soil characteristics at the EU level, or that specified at the particular national level).

(2) Conduct a limited analysis to compare the experimental location to the Tier 1 reference scenarios.

The first option can be considered using soil and climatic data as discussed in Section 7.2.5. The second option can be considered through comparison of the climatic data and soil characteristics of the Tier 1 scenario with the climatic data and soil characteristics of the lysimeter/field leaching study. Note that irrigation can be used as a substitute for higher rainfall.

In either situation, quantitative post-processing methods will still be necessary at the conclusion of the study to ensure that the anticipated climatic conditions etc had actually been met, as well as to incorporate the study design elements (such as duration).

8.3.4 Post processing approaches for higher tier experimental leaching data

8.3.4.1 Introduction

The guidance described below applies only to lysimeter studies. The work group is currently unaware of any accepted methods at the EU level for putting field leaching studies into a regulatory context. However the work group believes that such approaches can be undertaken in the future based on reasonable scientific principles by analogy to the process described below for lysimeter studies.

To address any issues about uncertainty in a limited experimental data set, all experimental data should first be checked to assess the expected vulnerability of the data. The approach

described below should be used. Soil specific DegT50 and K_{oc} values from the experimental data should be used (or in the absence of these data, the most favourable (highest) Kom and (lowest) DegT50 values from the experimental data set should be used) together with local meteorological data. The measured annual percolated amounts of water must be simulated reasonably well; otherwise the water flow should be calibrated (see work of Durner et al., 2008). If the predicted output with these parameters is >0.1 µg/L, then the lysimeter/field leaching result can be accepted for further assessment. If not the results of the lysimeter study are ignored because the conditions in the lysimeter study did not reflect adequately vulnerable conditions. If the proposed application rate is different from the application rate in the lysimeter, the 0.1 µg/L criterion is adjusted by multiplying by the application rate of the proposed use divided by the application rate in the lysimeter.

Example

A lysimeter study has been performed with application rates for parent P1 (2 x 0.2 to 2 x 0.25 kg as/ha in the lysimeter study) on winter cereals in climatic conditions of northern Germany. Experimental results of the lysimeter study with measured concentrations of metabolite M1 are given in Table 8-3. The simulated concentrations of M1 in the lysimeter soil and climate are stated in Table 8-4. The standard FOCUS ground water Tier 1 PECgw value for this GAP in the Hamburg scenario was 0.4 µg/L. In this case the lysimeter shows leaching <0.1 µg/L in conditions where simulations would have predicted >0.1 µg/L. Thus the lysimeter results could not have been predicted and can be accepted as valid for subsequent use in further assessment.

Table 8-3. Application rates of parent P1 and concentrations of M1 ($C_{LYSIMETER}$) in the lysimeter leachate.

	lysimeter A	lysimeter B	lysimeter C
Application rates of P1			
Application 1st year	2 x 0.25 kg as/ha	2 x 0.25 kg as/ha	2 x 0.25 kg as/ha
Application 2nd year			2 x 0.20 kg as/ha
M1 in leachate ($C_{LYSIMETER}$) [µg/L			
mean 1st year	0.03	0.04	0.04
mean 2nd year	0.02	0.04	0.09
Mean 3rd year	-	n.d.	0.01

Table 8-4. Predicted concentrations of M1 ($C_{SIMULATION}$) when the experimental conditions are input into a model.

	lysimeter A	lysimeter B	lysimeter C
M1 in leachate ($C_{SIMULATION}$) [µg/L			
Mean 1st year	0.06	0.06	0.08
Mean 2nd year	0.11	0.11	0.15
Mean 3rd year	0.01	0.01	0.04

In the next stage an inverse modelling (see Appendix 10 for the detailed theory of inverse modelling) of the leaching data set is conducted to derive important pesticide parameters of sorption and degradation (see Figure 8-9 for a general flow chart describing the inverse modelling procedure, although it should be noted that the particular process recommended in this report does not involve the use of a calibration step). These parameters are then used together with the existing data set to calculate refined input values for use in standard FOCUS scenarios. Inverse modelling has been introduced in pesticide fate modelling as a way to remedy to the pitfalls of classical parameter identification techniques (Casey and Simunek, 2001; Gottesbüren et al., 2001; Altman Dieses et al., 2002; Roulier and Jarives, 2003ab; Heistermann et al., 2003; Dubus et al., 2004; Larsbo and Jarvis, 2005). The availability of new advanced modelling techniques for the soil-crop system, together with the

availability of fast forward simulation models and optimisation algorithms, allow now the use of inverse modelling on a more regular basis. The choice of initial values, formulation of goal functions, target data, may have an effect on the inferred parameters and care has to be taken to describe the approaches and decisions as transparently as possible in order to make it reproducible.
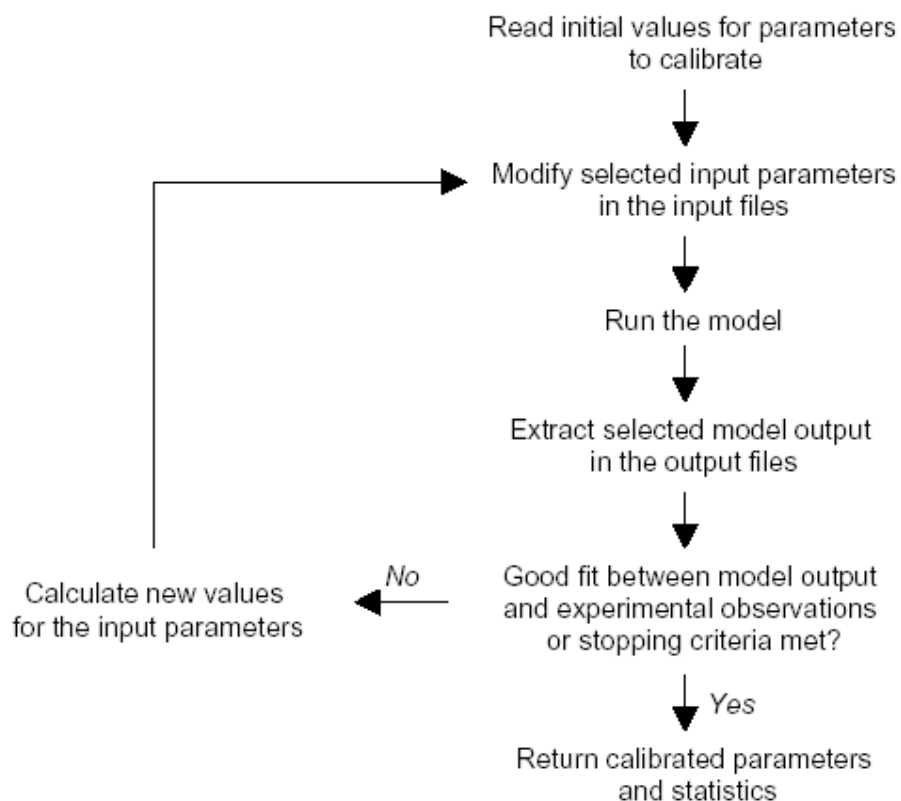
Figure 8-9. Flow charts describing the inverse modelling procedure (Dubus et al., 2000).

Inverse modelling cannot be based on a single soil core; as a minimum, measurements using duplicate soil cores taken from the same field are needed. In the following sections, the term 'lysimeter study' refers to a study with at least two soil cores taken from the same field.

8.3.4.2   *Proposed inverse modelling procedure for lysimeter studies*

The first part of the inverse modelling is a calibration step to adequately describe the soil hydrology of the leaching study, in terms of both temporal and total fluxes. In order to be able to evaluate pesticide behaviour, the water balance in the soil must firstly be correctly simulated. This should include a correct description of percolate volumes over the course of

time. If a conservative tracer was applied to the study, it must also be evaluated during the calibration phase.

Another prerequisite is that an inverse modelling technique has been applied that allows assessment of the uncertainty of the fitted parameters (see e.g. Mertens et al., 2009). This could also include information on response surfaces or probability density functions of the assessed parameters.

Inverse modelling studies with pesticide leaching from lysimeters have shown that there may be strong dependencies between e.g. the fitted Freundlich exponent and the fitted K_{om} or K_{oc} (e.g. Mertens et al., 2009). Similar strong dependencies can be expected between the fitted DegT50 on the one side and parameters describing effect of temperature, moisture and soil depth on degradation on the other side. Since the fitting is based on measured pesticide leaching at the bottom of a 1-m column, these parameters may have similar effects on the simulated leaching concentrations. Usually the soil residues of parent and metabolites that are measured in the soil cores of the lysimeter study at the end of the study after destructive sampling with very sensitive analytical methods (usually ^{14}C labelled compounds) could give valuable additional information. Measurements of residue distribution in the soil plough layer during the lysimeter study would also be helpful.

Mertens et al. (2009) could obtain narrow probability density functions for *DegT50* and K_{om} when they kept all other substance parameters constant. To ensure consistency in the risk assessment, all substance parameters that are not fitted, should be set to the same pesticide values used in the lower tier leaching calculation. These parameters include those describing the moisture, temperature and depth dependencies of degradation, the Freundlich exponent, long-term sorption parameters etc. The dispersion length should also be set to the 5 cm used in the lower tier leaching calculations (unless e.g. leaching of a tracer was measured as well in the lysimeter study, allowing the dispersion in the individual soil core to be estimated).

The above recommendation to use the same parameters as used in the lower tier calculations does not apply to soil properties of the lysimeter system that were measured at the end of the study (organic matter, texture and pH of the different horizons). For such properties and e.g. hydraulic properties derived from them, the measurements from the lysimeter should be used.

In the inverse modelling procedure, attention should be paid to the uncertainty resulting from initial loss processes at the soil and plant surfaces. For example, consider the case where pesticide is sprayed onto a crop and 50% of the dose is quickly photodegraded. If the inverse modelling procedure assumed that 100% of the dose penetrated into the soil, this would lead to a systematic underestimation of the *DegT50* in soil which is undesirable. The group proposes that a best estimate of photodegradation, volatilisation (based on the scientific information provided as part of the regulatory dossier) and interception (based on FOCUS, 2002 recommendations and consistent with the first tier approach) should be used to estimate the soil loading.

A resulting *DegT50* or K_{om} / K_{oc} value is acceptable for further use in the risk assessment if the lower limit of its 95% confidence interval is larger than 50% of the expected value from the inverse modelling procedure and if the upper limit is less than 200% of the expected value (so between a factor two lower and a factor two higher). When this criterion is not met, then the 75[th] percentile (more vulnerable) value should be used.

If the concentration in the leachate of the lysimeter remained always below the LOD or LOQ (usually in the order of 0.01 μg/L), then it is impossible to derive from the inverse modelling distributions with expected values for the *DegT50* or K_{om} parameters. Instead the inverse modelling will result in a *DegT50* - K_{om} line that divides the *DegT50* - K_{om} plane into two subplanes: one subplane gives the possible *DegT50* - K_{om} combinations and the other the impossible *DegT50* - *Kom* combinations (see line A in Figure 8-10). In this case, the K_{om} used in the lower tier assessment and the corresponding *DegT50* from the *DegT50* - K_{om} line should be used in the further assessment. This preference for estimating the *DegT50* from the lysimeter study rather than the K_{om} is based on the complications with respect to an inversely modelled K_{om} as described in Section 8.3.4.4.
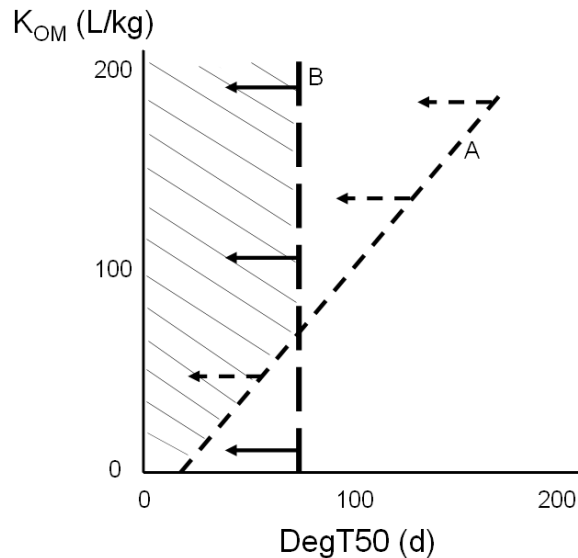
Figure 8-10. K_{om} – *DegT50* **diagram illustrating the restrictions resulting from an inverse modelling study based on a lysimeter study (A) with all concentrations in the leachate below the detection limit, and (B) with all concentrations in soil extracted at the end of the study below the detection limit. The shaded area shows the combined effect of the restrictions A and B.**

If at the end of the study, all total concentrations in the soil profile (extracted with organic solvent) are below the detection limit (usually in the order of 1 µg/kg), then the inverse modelling procedure probably will result in an upper limit of the *DegT50* (see line B in Figure 8-10). In such a case this *DegT50* should be used in the further assessment.

Note that *DegT50* or K_{om} / K_{oc} values obtained by the above procedure are of a different nature compared to lower tier *DegT50* or K_{om} / K_{oc} values: values obtained from a lysimeter study are effective values for leaching at 1 m depth, based on the behaviour in the top 1 m of soil.

8.3.4.3 *Further use of inversely modelled lysimeter DegT50 values in the leaching assessment*

The only risk assessment cases considered in this section are where lower tier simulation indicated a risk for ground water. Cases where lysimeters play only a confirmatory role, are not considered. All DegT50 values from laboratory, field persistence or lysimeter studies are assumed to reflect degradation rates within the soil (so no photochemical degradation at the soil surface) and that they have been normalised to 20°C and field capacity. All DegT50 values are also assumed to be based on the same description of degradation (so if non-equilibrium sorption is included all DegT50 values refer to the equilibrium part of the soil).

154

The procedure recommended below for the use of lysimeter DegT50 values in the leaching assessment has no thorough scientific basis. However, the problem is that a choice has to be made between alternatives. The work group considers these recommendations a reasoned compromise between (a) ignoring single lysimeter studies because they represent only one field, (b) giving a single lysimeter study infinite weight by letting its DegT50 overrule all previous DegT50's.

One case is where only DegT50 values from laboratory studies (e.g. four) are available together with one DegT50 from a lysimeter study. In this case, averaging to obtain an overall average DegT50 (lab and lysimeter) is inappropriate, because the procedure would be too uncertain to conclude on the risk of leaching to ground water. Therefore, in this case the results of the lysimeter study are ignored and the leaching assessment is based on lab studies.

Another case is where besides DegT50 values from laboratory studies and one DegT50 value from a lysimeter study, also DegT50 values from a number of field dissipation studies (e.g. four) are available. In this case field studies only are used and the laboratory data are discarded. The DegT50 from the lysimeter should be given three times the weight of the other DegT50 values. The argument for this is that DegT50 values from field persistence studies reflect the degradation rate in the top 0 - 20 (or 30) cm whereas a DegT50 value from a lysimeter study reflects the effective degradation rate in the top 100 cm. Moreover, the FOCUS ground water scenarios consider three layers in the top 100 cm for describing the depth dependency of the transformation rate. So using the above weighting procedure, the geometric mean DegT50 should be calculated and used in subsequent calculations.

Admittedly, the above recommendation has no thorough scientific basis. However, as stated before the problem is that a choice has to be made between alternatives. The work group considers our recommendation a reasoned compromise between (a) ignoring single lysimeter studies because they represent only one field, (b) giving a single lysimeter study infinite weight by letting its DegT50 overrule all previous DegT50's.

8.3.4.4 Further use of inversely modelled lysimeter K_{om} / K_{oc} values in the leaching assessment

The use of K_{om} / K_{oc} values obtained from lysimeters is not straightforward. For example, let us consider a case where batch adsorption studies with four soils resulted in K_{om} values

ranging from 20 to 35 L/kg. Furthermore inverse modelling of a lysimeter study (assuming only equilibrium sorption) generated a median K_{om} of 50 L/kg with a 95% confidence interval of 40 to 60 L/kg. The interpretation of such a discrepancy could be that the long-term sorption process in the lysimeter caused the higher "effective" K_{om} derived from the lysimeter. In such a case to applying some averaging procedure to the K_{om} assuming equilibrium sorption does not seem meaningful.

Given the above complication and given the very limited experience with K_{om} values obtained by inverse modelling from lysimeters in an adequate way, only a first proposal for guidance can be made here.

One approach could be to use K_{om} derived from lysimeter studies only if both in the lower tier and in the lysimeter tier long-term sorption kinetics were included. In such a case the same procedure could be justifiable as for the DegT50: give the value from the lysimeter study a weight that is three times the weight of the lower tier measurement with the same reasoning: the K_{om} from the lysimeter reflects the sorption behaviour of a 1-m thick soil layer whereas the lab studies only reflect the sorption in the top soil layer.

Since Section 7.1.6.4 recommends lower limits of the non-equilibrium sorption coefficient, including long-term sorption kinetics is advisable when estimating parameters from lysimeter studies by inverse modelling.

Figure 8-11 provides a summary of the inverse modelling procedure process for lysimeter studies. An example case illustrating this process is given in Appendix 11.
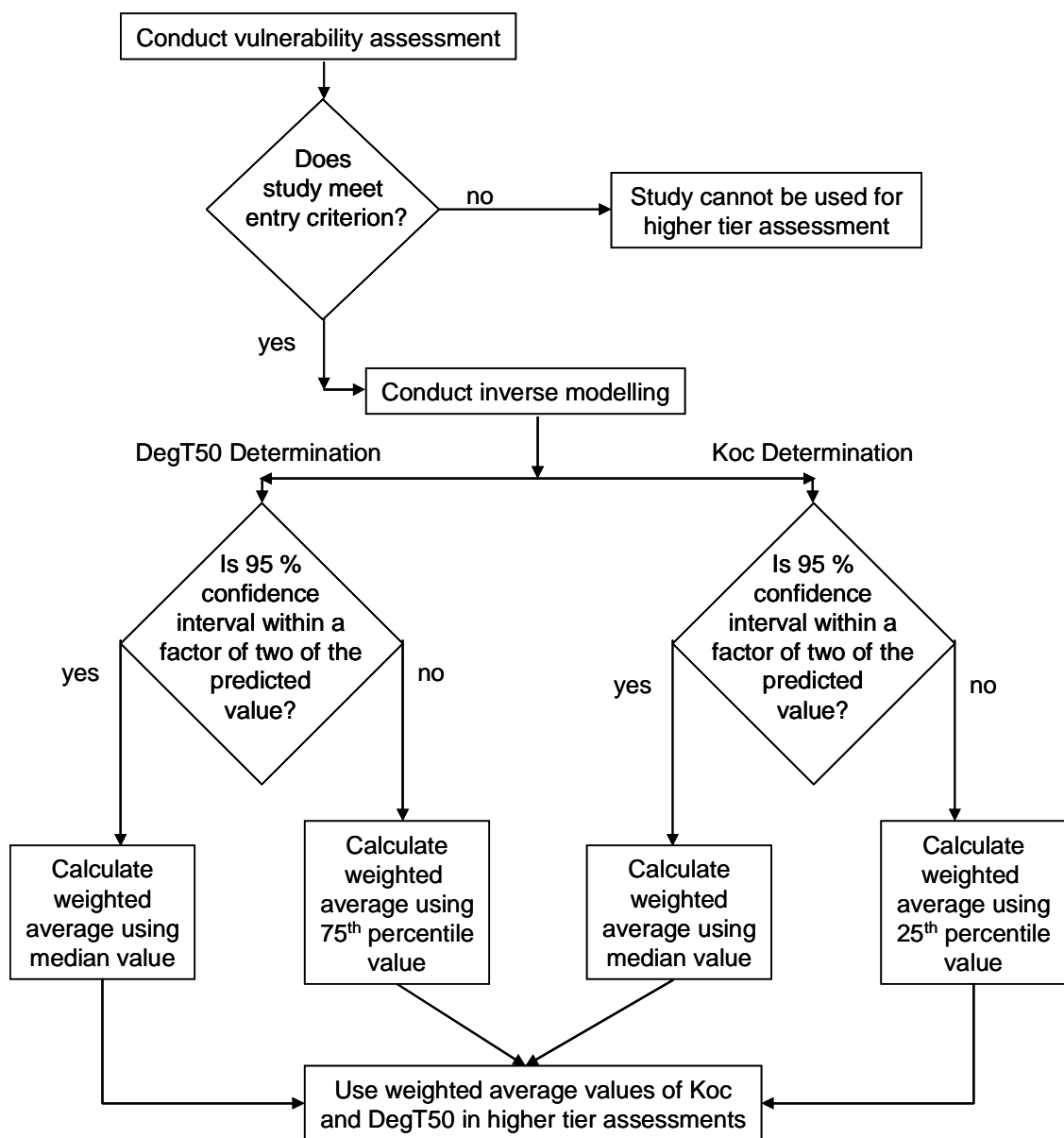
Figure 8-11. Flow diagram of the inverse modeling process for lysimeter studies.

8.4 Other modelling approaches (Tier 3d)

The current FOCUS modelling approaches for assessing exposure to ground water built on a series of hypothesis that have been described in detail by FOCUS (1995; 2000). One of the principle working hypotheses is that the flux of the active ingredient calculated at 1 m depth in the soil profile is a good indicator of the exposure to ground water. The flux at 1 m depth can therefore be used as a trigger for decision making within the framework of 91/414. Another principle working hypothesis is that the flux of the active ingredient for a location in Europe (e.g. the scenario location in Tier 1), can be assessed by means of a 1-D fate and

transport model for the soil, whereby the transport of the active ingredient in the soil is mainly considered as a chromatographic transport process. An exception to this working hypothesis is made when the preferential flow module in MACRO is activated (e.g. Châteaudun scenario calculations at Tier 1). The concept of homogeneous 1-D fate and transport in the soil is maintained when moving to the higher tiers. In Tier 2a improved parameterisation schemes of the 1-D FOCUS models are suggested. In Tier 2b and 3, the simulations are repeated with the 1-D models to cover in a more realistic way the variability of the soil-crop and climate properties at the larger scale.

Yet, the FOCUS models that are used in all aforementioned tiers suffer from a series of drawbacks that are related to conceptual modelling problems and problems of parameter and input estimation. The 1-D FOCUS models have been the subject of a set of experimental validation studies (see Chapter 6 of FOCUS; 2000 for references on recent validation studies) which should reduce the risk of conceptual bias. However, most of the validation studies so far pertained to the local scale (i.e. the lysimeter scale or the small field scale) and only few approaches have been reported to validate the predictions of the large scale exposure (Sulmon et al., 2006). The conceptual and parameter estimation problem (at the local and the larger scale) generate uncertainties in the final ground water exposure assessments. Uncertainties issues were already addressed in FOCUS (2000). The additional conceptual problem of applying local scale 1-D models to assess large scale exposure will not reduce this uncertainty.

In spite of these weaknesses, the work group estimates that the modelling approaches presented in previous chapters remain suitable for assessing movement of active substances to ground water within the framework of directive 91/414. Note however that new process knowledge on subsoil fate and transport is continuously generated, which may be introduced to improve ground water exposure assessment in the future. The following sections give an outlook of alternative approaches that could be considered in future ground water exposure assessment procedures

8.4.1 Alternative models for transport of active substances in the top soil
Validation studies have elucidated the problems of the chromatographic flow concept to model heterogeneous flow of active substances in the top soil (Vanclooster et al., 2000; Trevisan et al., 2003). Scientific evidence exists that heterogeneous flow (e.g. preferential flow) should be considered as the rule, rather than the exception (Jury and Fluhler, 1992; Flury et al., 1995). Given the limitations of chromatographic flow concept to describe heterogeneous flow, alternative transport models have been proposed for describing

chemical transport in soils (Vanclooster et al., 2005). These alternative models consider the variability of the fate and transport process due to structural variation in the flow domain (e.g. fast flow in large pores versus slow flow in small pores). The models can be ranked depending on the degree of explicitness with which the structural variability is considered in the model.

In a first class of models, the structural variability is embedded in a completely implicit way in the transport model. In this class, two asymptotic transport models, which cover the end-points of mixing in the soil, i.e. the complete mixing versus no mixing model, can be grouped (Flühler et al., 1996). The complete mixing model implicitly assumes that the mixing scale is much smaller than the scale of the transport process. Active substances applied at the soil surface will move as a homogeneous front through the soil profile. On top of this homogeneous movement, fast and slow displacements will occur which will smear out the chemical front and which will be determined by the hydrodynamic dispersivity of the soil. The current FOCUS models, except MACRO, belong to this class of models, and the harmonization of the hydrodynamic dispersion should result in consistent predictions of the leaching percentiles with this class of models.

In contrast to these so-called full mixing models, models have been developed which assume that the mixing scale is much larger than the transport scale. In this case, active substances in the soil will move through a set of isolated stream tubes and no mixing of the active substances between the stream tubes will occur (see early studies of Dagan and Bresler, 1983).

In the second class of models, the multi-domain models, the structure of the flow field is embedded in the model by dividing the porous medium in two (e.g. van Genuchten and Wagenet, 1989; Larsbo and Jarvis, 2003; Gerke and van Genuchten, 1993) or more (Steenhuis et al., 1990; Skopp and Gardner, 1992; Durner and Fluhler, 1996; Durner et al., 1999) sub-domains in which active ingredients move at different velocities. Between the sub-domains chemicals are exchanged by diffusion and/or advection. The exchange rate is a fitting parameter, which can be related to some extent to the structure and spatial scale of the different flow domains. The MACRO model is an example of such a multi-domain model, and could be applied to model heterogeneous flow if parameterisation issues are resolved.

In the third class of models, the structure of the porous medium is characterized in a geo-statistical sense. By solving the stochastic-continuum flow and transport equations, the lateral solute mixing and the mixing time are derived from the spatial distribution of

macroscopic hydraulic properties. In all previous classes, effective vertical 1-D transport is considered to occur in the soil.

In the fourth class of models, the structure of the porous medium is explicitly considered and 2 or 3-D flow and transport processes, either at the pore or the macroscopic scale, are solved in a medium with known structure. When the structure of the medium is identified, the flow and transport processes may be predicted without any fitting of flow and transport parameters (Vogel and Roth, 2003). Different numerical solvers for the 2 and 3-D unsaturated flow and transport problem are readily available (see e.g. Simunek et al., 1995).

8.4.2 *Modelling fate and transport of active substances in the partially saturated subsoil*

The FOCUS modelling approach considers the exposure at 1 m soil depth as a conservative estimate of the exposure to ground water. Yet, in many cases, vulnerable ground water systems are situated deeper in the subsoil and active ingredients passes through a partially saturated vadose zone before the ground water body is reached. In this case, additional dispersion, sorption and degradation will determine the real exposure to the ground water system.

As a first approximation, the existing FOCUS models are suggested to be used to consider processes in the subsoil by extending the modelled soil profile. Roulier et al. (2006) for instance studied atrazine transport through a fractured deep limestone covered by a luvisol and calcisol in France by means of the MACRO model. They suggested that the thickness and properties (e.g. matrix versus fissure flow) of the limestone will only have a small effect on the long term atrazine leaching, since atrazine is a rather mobile substance and degradation is low in the limestone.

As an alternative to the existing FOCUS models, the more advanced approaches presented in the previous section could also be used to model the subsoil fate and transport. In most cases however, little information, if any, on the transport, sorption and degradation properties of the deeper subsoil is available. Therefore, 1D modelling approaches or even simplified and empirical models are mostly adopted to model transfer of active substances from the bottom of the soil to the top of the ground water body. Spurlock et al. (2006) coupled the PRZM model for the top soil with a semi-empirical transfer model to predict ground water loading in the San Joaquin valley, California. For the same ground water body, Stewart and Loague, (1999) used simplified linear transfer function theory (Jury and Roth, 1990) to model transport through soil and sub-soil.

8.4.3 Modelling fate and transport of active substances in the soil and ground water continuum

Adopting a holistic view, substance fate and transport can be modelled through the soil and ground water continuum. The explicit introduction of the ground water body in the modelling system changes its dimensionality, since flow and transport in ground water bodies is merely horizontal rather than vertical. It also allows the consideration of specific ground water processes on the final exposure to specific targets. Hoiberg et al., (2005) for instance modelled transport and fate of three herbicides in an aerobic aquifer with variable pH. They showed that a pH dependent degradation rate in the ground water body was needed to explain the observed concentrations during a controlled pesticide tracer experiment.

Two approaches can be distinguished for modelling substance fate and transport in the soil-ground water continuum: loosely coupled approaches and fully integrated approaches. In the loosely coupled approach, the 1-D soil – subsoil model is used to define the upper boundary condition of a ground water flow and transport model. Tiktak et al. (2005) for instance coupled the FOCUS PEARL model to a regional ground water model to assess substance transport in Dutch ground water bodies. Stenemo et al. (2005) coupled the FOCUS MACRO model with a ground water model for fractured till. In this case, the linking procedure (macro pore versus fracture) had a significant effect on the modelled substance behaviour in the ground water body itself. They also showed that considerable differences are obtained between steady- state and transient flow simulations. For assessing exposure of local point pollution, Aivalioti and Karatzas (2006) illustrated the linking between a spatially distributed version of the FOCUS PRZM model with a 3D ground water flow and contaminant transport model.

In the fully integrated approach, the same flow and transport equations are solved as well for the saturated (i.e. the ground water body) as for the partially saturated (the soil and subsoil) system using numerical solvers. Mouvet et al. (2004) compared loosely and fully coupled approaches to assess substance fate and transport in different aquifers in Europe. They concluded that the fully coupled models were more appropriate than the loosely coupled 1-D model to assess ground water exposure. Boivin et al. (2006) applied a fully coupled model to assess the transport of bentazone in a tile drained field in France. They showed that outflow (drainage and deep percolation) in this system could only be modelled by considering the 2D flow and transport process in the field. They also showed that a reasonable matching of the drain outflow could only be obtained when preferential flow was considered in the 2D model and when local parameters were fitted. Even if the drain flow is merely of concern for surface water emissions, the simulated deep percolation and hence the emission to ground water

was affected by this parameterisation strategy. At the regional scale, Herbst et al. (2005) modelled isoproturon behaviour by means of the fully coupled TRACE/3DLEWASTE model. The modelling results were consistent with the observations found in monitoring wells and allowed in particular to elucidate the specific role of the vadose zone in calculating ground water loadings.

8.4.4   Statistical modelling of monitoring data

The highest tier proposed in this report considers monitoring data as a trigger for decision making. As mentioned in Chapter 9, monitoring data are unlikely to be available for new active substances prior to a decision on suitability for positive listing. Therefore, monitoring data will only will be available for consideration at the Annex I level for existing active substances.

If monitoring data are available that comply with the required quality standards (see Chapter 9), than statistical modelling techniques can be used to predict pesticide in ground water bodies at the large scale based on local scale monitoring data. Sahoo et al. (2005) used substance data collected from 124 domestic wells to predict substance concentration in the ground water body using artificial neural network models. They considered land use and sampling well indicators as model predictors. By means of cross validation techniques, they obtained modelling efficiencies which were larger than 85 %. They also illustrated that the depth of the wells were an important predictor in the model. Geo-statistical techniques offer another alternative for making space-time predictions of pesticide concentrations for large ground water bodies. Yet, the available monitoring networks are in generally very coarse, which may result in large nugget effects and small correlation lengths, and therefore large uncertainties in the spatial predictions with geostatistical techniques like kriging (Leterme et al., 2007a).

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9   APPROACHES FOR THE USE OF GROUND WATER MONITORING DATA AT TIER 4

The phrase "monitoring study" is frequently used and can cover a variety of methodologies. At the outset it is appropriate to clarify what the principle approaches are and Lee (1996) has determined three types of study that are used in the USA:

> *(a) Large scale retrospective studies: The objective of these studies is to characterize the extent of occurrence of pesticides in wells over a large area. These surveys typically involve sampling of more than 100 wells.*

> *(b) Small-scale retrospective studies: These studies are carried out in a field in which a pesticide(s) has been used over a period of time and are used to determine whether the pesticide(s) in question has leached to groundwater in certain fields and to characterize the leaching pattern in the soil profile at a given point in time. The minimum number of well sites is about four for each study site.*

> *(c) Small-scale prospective studies: These studies are usually associated with the pesticide use registration process and their primary objective is to characterize the subsurface fate of a particular pesticide i.e. controlled study.*

Within the scope of the current document however, the small scale prospective studies are considered as a variation of a field leaching study. This is because they are controlled experiments in which the pesticide application can be directly linked with residues moving to the ground water. They also concentrate on obtaining detailed experimental process data on a relatively small number of sites (typically 2-3) rather than at a larger scale. For those interested in the conduct of these studies, guidance has been provided by the US EPA (1998). Further, the distinction between large scale and small scale retrospective studies is not helpful in an EU context.

Therefore, within the context of this document monitoring studies are defined as:

> *Studies in which ground water is sampled from a large number of locations in a region or country and is subsequently analysed to determine the concentration of the pesticide or metabolite of interest. Experimentally determining the reason for the presence or absence of the compound is not necessarily an intrinsic part of these studies, although the weight which is placed on the findings will depend on the appropriate selection of the sites to sample*

Concerns about the potential of an active substance to reach ground water at concentrations in excess of 0.1 µg/L may be raised during the lower tiers of risk assessment in a regulatory

evaluation of a new or existing substance (either at the Annex I listing stage or the national product registration under Directive 91/414/EEC). However, monitoring of ground water in the EU is routinely undertaken by water companies and government bodies (often to comply with other EU legislation) and this may also lead to a concern that particular existing pesticides and/or metabolites have been detected in ground water in excess of 0.1 µg/L.

The intention of this chapter is to provide some guidance on how best to use existing monitoring data and how to most effectively generate new monitoring data in cases where the leaching risk is considered not to have been sufficiently clarified by the simpler (lower tier) stages of the assessment.

9.1 Sources of ground water monitoring data

Broadly speaking ground water monitoring data can be differentiated into three sources:

1. Dedicated monitoring studies conducted by the notifier in response to a specific regulatory request (generally following detailed discussions with the relevant regulatory authority)
2. Proactive targeted monitoring studies conducted by the notifier
3. Monitoring data conducted by third party organisations for purposes other than authorisation under Directive 91/414/EEC (e.g. by environmental agencies concerned with water quality). This information may be collated and submitted by a notifier together with a justification of the results obtained. However, ground water monitoring data can also be directly submitted by a third party or the regulators may become aware of data via other sources than the notifier (e.g. from publications, presentations etc).

In each case, the focus of the work is subtly different and hence the applicability for regulatory decision-making may not be equal in all cases. For instance source 1 relies heavily on the prior discussion with the relevant regulatory authority, with an expectation that the remit of the work and methodology have been specifically agreed and the decision-making criteria are clearly understood prior to the initiation of the data collection. Source 2 would result in the notifier conducting their own studies, presumably using a dedicated analytical method for the compound of interest. The notifier would control which sites are sampled and would have the opportunity to construct a coherent strategy of timing and location within the context of Directive 91/414/EEC that they can scientifically justify to the regulator. For many existing pesticides, source 3 will be the largest available source of information on actual concentrations in ground water and hence has the potential to contribute significantly to the scientific decision-making process. However, as the data are not generated specifically for the requirements of Directive 91/414/EEC, they are likely to be

rather less focused to that legislation. Data may be multi-residue analyses with less attention given to false negatives or false positives, they may be from less relevant areas (e.g. where the pesticide is not used in agriculture) or they may be targeted to known spills or point-source contamination. Therefore, the quality and relevance of these data must be assessed before regulatory decision-making. Some potential issues are highlighted by Leterme et al. (2006) and Schmidt et al (2005). The emphasis of the regulation is rightly on the notifier to demonstrate that safe use of the pesticide can occur. Therefore, logically the notifier should be initially tasked with this assessment of relevance, once the data has been made available to them.

9.2   Existing national guidance

Certain member states such as the UK (Mackay et al., 2004), the Netherlands (Cornelese et al., 2003), and Germany (Aden et al., 2002) have already published guidance on the use of monitoring data in pesticide registration. At this time the work group is aware of no other publications of national approaches.

The UK guidance notes the potential of monitoring studies to determine the actual leaching to ground water, but focuses mostly on the difficulties of obtaining high quality data from such analyses.

The German national guidance makes a clear distinction between addressing adverse findings from other sources of ground water monitoring data (i.e. source 3; in the case of existing pesticides) and the possible need for the authorisation holder to undertake dedicated post-registration monitoring studies (i.e. source 1, for both new and existing active substances) in the case that the available data are insufficient to determine the real risk to ground water during evaluation. When adverse monitoring data from source 3 (e.g. water companies, etc.) are obtained, there is an obligation for the authorisation holder to further investigate each of the positive detections and determine (if possible) the cause (e.g. analytical error, cross contamination of sample, contamination of borehole, misuse of pesticide, use of pesticide within GAP etc). Where the regulatory authority requires post registration monitoring, the guideline requires that studies should be undertaken at a number of sites with sampling at least monthly over at least 4 years. No clear criteria are given for subsequent decision-making on the basis of these results.

In the Netherlands two separate forms of ground water monitoring are recognised; those in upper ground water (< ca 5 m depth) and those in deeper ground water (ca 10 m depth).

174

Consistent with the terminology of this chapter, studies in the upper ground water could be considered as a form of a field leaching study since the link between pesticide application and concentration in the upper ground water is specifically stated in the Dutch guidance. Therefore this type of "monitoring" is not considered further in this chapter, except to note that the broad requirements for this type of study are stated to be: 8-10 fields with 12-20 sample locations/field and 3 time points (before, during and after the simulated peak concentration).

The existing Dutch guidance for the deeper ground water monitoring proposes single samples from ≥100 permanent wells. The applicant must provide these data although some or all of these data points could be provided from source 3 (see sources of ground water monitoring data), if the stated detailed quality criteria are met. General guidance is provided on selection of appropriate locations/wells and subsequent exclusion of false negative and positives. The hypothesis to be tested is that the 90th percentile in space of the long-term average concentration in ground water at 10 m depth exceeds 0.1 µg/L. Since the ground water tested will have been formed in a number of different years (due to the range of hydro-geological conditions), the approach considers that the "variability in long term climatic conditions will be accounted for in the sample population". In turn this means that a monitoring program does not need to be undertaken over any significant length of time. However, once the data are obtained, the implication is that a statistician still would be required to determine whether the hypothesis is met or not.

9.3   FOCUS guidance for EU level

At the EU level (Annex I listing) monitoring data is unlikely to be available for new active substances prior to a decision on suitability for positive listing. Therefore, monitoring data only will be available for consideration at the Annex I level for existing active substances.

The FOCUS proposal (as stated in Chapter 4) is that where such data are available, whether generated by the notifier or other organisations, they can be used for decision-making subject to certain quality checks.

The criterion for an Annex I listing is that "a safe use" exists within the EU. Sufficient data of acceptable quality must be available to determine that a safe use exists. This is likely to take the form of absence of positive detections of pesticide, despite it being analysed for with an appropriate limit of quantification. The FOCUS ground water scenarios aim to be at the 90th percentile vulnerability and FOCUS (2000) have considered that passing any one of these

nine crop/location combinations would constitute a "safe use" To maintain a degree of scientific consistency in the risk assessment process, FOCUS therefore recommend that available monitoring data would need to be from significant agricultural regions (similar to the terminology of FOCUS, 2000) where the active substance has history of use. Further, the work group proposes that 90% of analyses, obtained from at least 50 locations (a location is defined as a single well or group of wells at the same site) would need to be <0.1 µg/L in order to grant Annex I listing (if the data come from source 3 and are unfocused). A smaller number of locations (ca 20) would be acceptable if they are specifically targeted to the pesticide of interest from source 1 or 2. The work group recognises that there is no statistical basis for these numbers of locations. However they are broadly consistent with the existing Dutch (and US) national guidance and are considered to provide a proportionate data burden for this final risk assessment step in comparison to the earlier steps. In common with the Dutch national guidance, the work group believes that sampling does not need to be carried out over an extended period of time. However, the design strategy based on a single sample is not appropriate if the ground water is greatly influenced by surface water, as when large wells are located near streams.

When considering the appropriateness of each location, several agronomic, climate, pedologic and hydrogeological aspects need to be examined. These include: history of compound use, vulnerability of soil type, depth of sampling point, and aquifer type representativity. The locations should be distributed throughout the region. Comparing results to simulation modelling may also be helpful when considering the relevance of the location. In summary, the quality and the representativity of the monitoring must be appropriate for the intended use under consideration

9.4   FOCUS guidance for national level

At the national level considering the protection goal and how to scientifically determine whether the goal is achieved is even more important.

FOCUS considers that designing a monitoring program to scientifically and statistically test the hypothesis provided by the protection goal is necessary at the national level. Therefore, although monitoring data from source 3 (see sources of ground water monitoring data) may still be acceptable on grounds of quality criteria, it is necessary to check if sufficient sites are appropriately situated in order to test the specific hypothesis solely on the basis of these data.

Note post-approval monitoring is not currently acceptable within the regulatory framework in some countries (i.e. UK). This could therefore cause difficulty for assessment of new active substances in these Member States.

9.5   Quality criteria

FOCUS proposes that appropriate quality criteria for data are as follows. These are partially based on those provided by Cornelese et al. (2003) as well as on internal discussion:

1. Data are from areas where the active substance has been used for a long period of time and is being used during the sampling period
2. Soils in study areas should be hydrologically connected to the ground water
3. Sampling analysis and documentation techniques must correspond to the current state of technology (i.e. excluding possibility of contamination during analysis and using analysis methodology that is sufficiently specific for the compound). e.g. to exclude false positives and false negatives
4. Contamination of borehole must be excluded. There should be proper rinsing and purging prior to sample collection
5. Removal of ground water should not be of too high a quantity to avoid withdrawal of water from other than the desired depths
6. Limit of quantification should be below 0.1 µg/L

Monitoring data from source 3 (see sources of ground water monitoring data) will generally be less targeted to the requirements of regulation than that from dedicated studies by the applicant. However, this is considered acceptable as long as the data conform to the minimum criteria given above and have been subject to critical scrutiny.

Dedicated monitoring studies for Directive 91/414/EEC (i.e. sources 1 and 2; see sources of ground water monitoring data) can be expected to conform to tighter regulatory standards and these may include compliance with GLP, more extensive documentation of sampling methodologies and analysis technique, etc.

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10 GUIDELINES FOR REPORTING OF HIGHER TIER LEACHING ASSESSMENTS

The intent of this chapter is not to prescribe how a higher tier leaching assessment should be inserted into a registration dossier, but only to indicate what needs to be reported in such an assessment, whether part of another report or as its own separate report. The nature of the report as well as the background information that needs to be included will depend on the study and the specific assessment.

The sections of a higher tier assessment report dealing with modelling should follow the fundamental principle of good modelling practice that enough information should be provided to allow independent replication of the results. Good modelling practices have been discussed in more detail by FOCUS (1995) based on the information in Estes and Coody (1993) and Görlitz et al. (1993).

10.1 Description of assessment

A report describing a higher tier assessment should always include introductory material clearly stating why the higher tier assessment is being performed and which tier the reported assessment addresses. When user developed scenarios are substituted for standard EU Tier 1 or national scenarios, this should be clear to the reader and the reason for the substitution justified. When using advanced and/or not commonly used assessment techniques, the assessment report must provide transparent descriptions of the method that can be understand by reviewers of the document. There is a special need to make transparent descriptions of the method in such a way that you do not need to be an expert within that specific field. Assumptions made in the performance of the assessment should be listed and justified, although the report does not have to provide and justify routine assumptions, such as those associated with the standard FOCUS models.

10.2 Data and input parameters

All values of input parameters not included as part of a standard scenario need to be provided in the report. This includes but is not limited to pesticide parameters, soil properties, and crop information. The selection of key parameters such as pesticide degradation rates and sorption constants should be described with appropriate references to the study reports. If the study reports are not available elsewhere in the dossier, then the

relevant material must be made available to the reviewer, perhaps as an appendix to the study report. If data from field dissipation or leaching studies are normalised to standard conditions, this procedure must be described either in the study report, a separate report, or the higher tier assessment report. The relevance of all laboratory and field studies used in a higher tier assessment should be assessed

Listing of multiple years of weather data or data layers used in GIS procedures is usually impractical. For commonly available data bases, a reference to the data base is usually sufficient. Any treatment of original data needs to be described and justified. For weather data not part of standard packages, providing location coordinates and an appropriate summary may be helpful to the reviewer. Also some provision may need to be made to provide information to the reviewer in a format such as a CD when needed to permit the reviewer to replicate the assessment.

10.3 Components of a higher tier assessment

The report should address the following aspects of the assessment:
1. Explain the need for the higher tier assessment and justify the approach taken.
2. Provide a transparent description of the methodology used. If the procedures used are not standard methodology, the descriptions need to be detailed and should include references to any work performed to demonstrate the validity of the approach.
3. Provide the name and exact version of all models and software packages used. If models used have not been included in FOCUS (2000, 2006), detailed descriptions need to be provided along with references to work performed to demonstrate the validity of the model.
4. Describe for which agricultural areas the higher tier assessment is relevant.
5. Provide in the report a summary section, which describes the assessment step by step in a way that is understandable by evaluators having a scientific skill but not necessarily having the expert skill within the fields of higher tier leaching assessments.

All kinetic evaluations performed as part of a higher tier assessment should be conducted and reported as outlined by FOCUS (2006).

10.4 References

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11 REVIEW AND CHANGES TO EXISTING FOCUS GROUND WATER SCENARIOS AND CALCULATION PROCEDURES

As mentioned in Chapter 1, the remit for the work group included a providing a revised set of scenarios and leaching models. This task included the re-evaluation of the Porto and Piacenza scenarios, and harmonisation of the dispersion length and water balance among the models. This chapter deals with changes to PEARL, PELMO, and PRZM. Changes in MACRO will be addressed later.

The activities of the work group in revising the scenarios can be grouped into four areas. First a vulnerability concept had to be defined since there was a difference between the concepts used in FOCUS (2000) and APECOP (Vanclooster, 2004). This is described in Section 11.1. During this discussion the methods for calculation of the 80[th] weather percentile concentration were reviewed. The procedure recommended by the work group is described in Section 11.2. Using the vulnerability concept, modifications in the soil properties were proposed for the Piacenza and Porto locations (Section 11.3). The harmonization of the dispersion lengths was an issue that was not resolved by the FOCUS (2000). As stated in the remit, PEARL calculates leaching concentrations that are at least one order of magnitude higher than PRZM/PELMO if concentrations are close to 0.1 µg/L and dosages are in the order of 1 kg/ha. Determining the appropriate dispersion length was a difficult task for this work group and the results of this discussion are presented in Section 11.4. The harmonization of the water balances (described in Section 11.5) was also a difficult task because of the different descriptions used in the models for the various processes, such as runoff and evapotranspiration. The work group also reviewed the crop interception routines and decided not to make any changes (Section 11.6)

11.1 Proposal of a vulnerability concept for FOCUS scenarios

Each Tier 1 FOCUS GW scenario is intended to be a reasonable worst-case for leaching within the climatic zone that it represents and is a physical site known to exist, i.e. the combination of crop, soil, climate and agronomic conditions are realistic. FOCUS (2000) defined the reasonable worst-case for leaching as the 90[th] percentile, which in turn was defined as the combination of 80[th] percentile soil and 80[th] percentile weather. The leaching vulnerability was therefore defined by the characteristics of the scenario (intrinsic vulnerability) rather than by the combination of scenario characteristics, substance properties

and cropping etc (overall vulnerability)[13]. The vulnerability concept used by FOCUS (2000) for the Tier 1 scenarios is intended to approximately identify the 90th percentile leaching within a climatic zone for a broad range of substances, such as substances A- D in FOCUS 2000, but there may be exceptions for substances having different behaviour[14].

Under FOCUS (2000) 125 ground water leaching scenarios at nine locations have become established. A study designed to check vulnerability of the soil and weather associated with the nine locations using a regionalized modelling approach (Vanclooster et al., 2003) showed that the Porto and Piacenza locations did not represent the 80th percentile soil and weather for the relevant climatic zone. The parameters associated with these locations therefore need to be re-evaluated. For the purposes of this re-evaluation, we propose to consider the 90th percentile leaching vulnerability for the **climatic zone** represented by the Porto and Piacenza locations. In addition, we define the basic spatial unit for leaching as the soil mapping unit (defined by available data) and the basic temporal unit as an annual average for annual applications. Once this re-evaluation has been done, the weather and soil properties associated with the nine locations will represent a set of 80th percentile soil and weather values, one for each of the **climatic zones** established by the original FOCUS groundwater group (FOCUS, 2000). This implies that, within the context of this vulnerability definition, the climatic zones are defined on the basis of the EU of the 15 Member States so that the addition of new member states does not require the whole set of scenarios to be revised.

The purpose of the Tier 1 FOCUS scenarios is to establish whether a safe use exists within Europe. There has been considerable experience of using these scenarios for European registration, and some member states have adopted scenarios in their Tier 1 national evaluations for ground water. Given the legacy of decision-making with these sets of soil and weather data (7 out of 9 are unchanged), and in order to maintain continuity in the decision-making process, the work group strongly recommends that changes to this set of scenarios be only made in the light of compelling evidence that decisions on leaching risk are no longer credible. In particular, the addition of new member states should not require the whole set of scenarios to be revised. Instead, the applicability of the original scenarios to conditions within the new member states should first be established on the basis of the above concept,

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13 See Appendix 12 for a discussion on how a theoretical vulnerability criterion could be constructed from a basis of perfect knowledge of leaching
14 For example FOCUS (2000) assumed implicitly that the sorption of all substances is correlated to the organic matter or organic carbon content. Therefore substances whose sorption is correlated to other soil properties (e.g. pH, sesqui-oxides or clay minerals) may need evaluation outside of the Tier 1 scenarios.

and sets of soil and weather data for additional locations defined only if significant agricultural areas are not covered by the existing scenarios (for example see Section 11.2.1 on scenarios for new member states).

11.2 Determining the 80[th] percentile weather concentration

After reviewing several approaches (as described in Appendix 13), the work group decided that the 80[th] percentile weather concentration would be the average of the 16[th] and 17[th] ranked values from the simulation. In the previous simulations, the 17[th] ranked value was used.

For applications made every second or third year, FOCUS (2000) recommended calculating flux weighted averages for each of the 20 two or three year periods and then selecting the 80[th] percentile of these 20 values. The work group investigated taking the 80[th] percentile of the 40 or 60 yearly values. Because the two methods gave similar values (see Appendix 14), the work group recommended continuing with the calculating the 80[th] percentile of the 20 flux weighted averages.

11.3 Review of the Porto and Piacenza FOCUS ground water scenarios

A review of the Porto and Piacenza scenarios (Appendix 15) indicated that a change in the organic matter was appropriate to make them fit the vulnerability concept described in Section 11.1. The organic matter in the surface soil at Porto was decreased from 6.6 to 2.45 percent, resulting in changes to the bulk density, hydraulic properties, and the organic matter in the lower soil layers. The organic matter in the surface soil at Piacenza was increased from 1.72 to 2.17 percent, along with changes to the organic matter in lower soil layers. A comparison of current and proposed soil properties for each soil layer are provided in Appendix 15.

11.4 Harmonisation of dispersion lengths

One of the remits of the work group was to harmonise the dispersion lengths in the four models when used to assess concentrations in ground water for Tier 1 in the EU registration process. In simulations conducted according to the procedures in the previous work group

(FOCUS, 2000) PEARL and MACRO used a dispersion length of 5 cm and the effective dispersion length (set by compartment size) in PRZM and PELMO was 2.5 cm. Later work by Boesten (2004) showed that the difference in dispersion lengths was a major source of the difference between predictions of PEARL and PELMO or PRZM.

Dispersion classically is used to describe the width of the peak in chromatographic flow with the higher the dispersion the broader the peak. However, since flow in soils is not perfectly chromatographic, currently dispersion is used as a pragmatic approach to lumping the field variability of all processes that affect solute transport.

The vulnerability concept presented in Section 11.1 states that the 80[th] percentile soils in the region are desired. In the selection of the soil meeting the 80[th] percentile, the dispersion associated with each soil under the range of agricultural practices must be considered. The only exception is for heavier soils with impermeable subsoils (typically drained), which are not considered because the water in the soil profile is usually discharged to surface water rather than ground water. The main transport process associated with these soils is macropore flow.

Work group members undertook several activities associated with dispersion. This included a literature review of dispersion lengths associated with experiments conducted with inert tracers in soils (presented in Appendix 16). Using this information, two different approaches were developed. One approach, described in Appendix 16, approximated the dispersion predicted by two-dimensional simulations assuming heterogeneous water flow using a constant value for dispersion length with the convection-dispersion equation (CDE) for evaluating leaching at 1 m depth. The other approach divided the upper meter into three layers (corresponding to the different default degradation factors) with increasing dispersion lengths as a function of depth (Appendix 17). Both models were calibrated to provide the same breakthrough curve of an inert tracer at a depth of 1 m.

The work group discussed both approaches and could not come to a consensus. However, because of the need for harmonisation, the constant CDE approach with a dispersion length of 5 cm will be used in the revised scenarios produced by the work group. The constant CDE approach is the more conservative of the two approaches, at least for parent compounds.

Advocates of the constant CDE approach cited the better match to the predictions of the two-dimensional transport model and the more conservative approach for parent compounds.

Advocates of the layered CDE approach noted the better match in the upper 30 cm where the degradation rates were the highest and questioned the need for additional conservatism.

11.5 Harmonisation of the water balance

One of the objectives of the work group was to harmonise the discrepancies in the water balances obtained with the various models. Examination of these differences led to discussions in several areas: the most appropriate source of potential evaporation data, the importance of time varying crop Kc values, calculating evaporation from bare soil, determining appropriate amounts of runoff for each location/crop location and how to achieve this with the different models, and developing appropriate irrigation files for each location/crop location in the four locations where irrigation is a common agricultural practice. In addition to harmonize evapotranspiration the maximum rooting depths of some crops in certain locations needed to be changed.

11.5.1 Calculation procedure for evapotranspiration

Because of differences between potential crop and soil evapotranspiration predicted for certain location/crop locations between the FOCUS models, the work group reviewed the procedures used to calculate evapotranspiration. This included the appropriate source of reference evapotranspiration data, harmonising the use of crop kc factors within the models, and how best to harmonise the calculation of soil evaporation losses when no crop is present.

11.5.1.1 Comparison of MARS and FAO reference evapotranspiration

FOCUS (2000) used reference evapotranspiration calculated from the MARS data base and FAO crop coefficients. The work group examined whether FAO or MARS reference evapotranspiration was most appropriate (Appendix 18). The work group decided to use FAO reference evapotranspiration for Porto, Piacenza, Châteaudun, Thiva, and Sevilla for consistency between the crop coefficients and reference evapotranspiration values. The MARS approach to calculating reference evapotranspiration was retained for Okehampton, Kremsmünster, Hamburg and Jokioinen because there was little difference between the two approaches for these climatic conditions and the long wave radiation parameterisation procedure proposed by the FAO sometimes leads to negative reference evapotranspiration rates in northern European conditions.

11.5.1.2 Estimated crop kc factors

A comparison of the actual evapotranspiration showed that the different procedures within the models for implementing crop kc factors were contributing significantly to the variability of

the overall water balance. Therefore the work group decided to harmonize the procedures by implementing a common procedure in which the year was divided into four periods, and a constant kc factor assumed for each period. The procedures used in determining the crop kc factors are described in Appendix 19. For winter crops in the six locations (Châteaudun, Hamburg, Jokioinen, Kremsmünster, Okehampton, and Piacenza), a spring point (the date in the early spring or late winter when crop growth begins increasing at a more rapid rate due to the warming of the soil) was also assigned for use in PEARL to avoid excessive plant growth in the winter. For all of the crop/location combinations with a spring point, between emergence and the spring point, the LAI increases from 0 to 0.1 and the rooting depth increased from 0 to 0.2 m. Between the spring point and the time of maximum LAI, the LAI increases from 0.1 to its maximum value and the rooting depth increases from 0.2 to its maximum value. The resulting kc factors and time intervals and spring points are provided in Appendix 20, which defines the crop and soil parameters associated with each of the scenarios.

11.5.1.3 Evaporation from bare soil

A review of the amounts of actual evapotranspiration indicated that the amount predicted by PEARL was systematically lower than that predicted by PELMO and PRZM at three locations (Piacenza, Sevilla, and Thiva). Because the largest difference was observed with Thiva cabbage, this scenario was investigated in more detail. The period chosen for investigation was a dry period following a period of rainfall sufficient to bring the soil up to field capacity. The cumulative evapotranspiration from the three models is shown in Figure 11-1. PRZM (30) and PELMO (30) show very similar evapotranspiration losses while PEARL shows lower evapotranspiration beginning on April 26 (three days after the last rainfall). These differences are the results of the different models used to estimate soil evaporation.
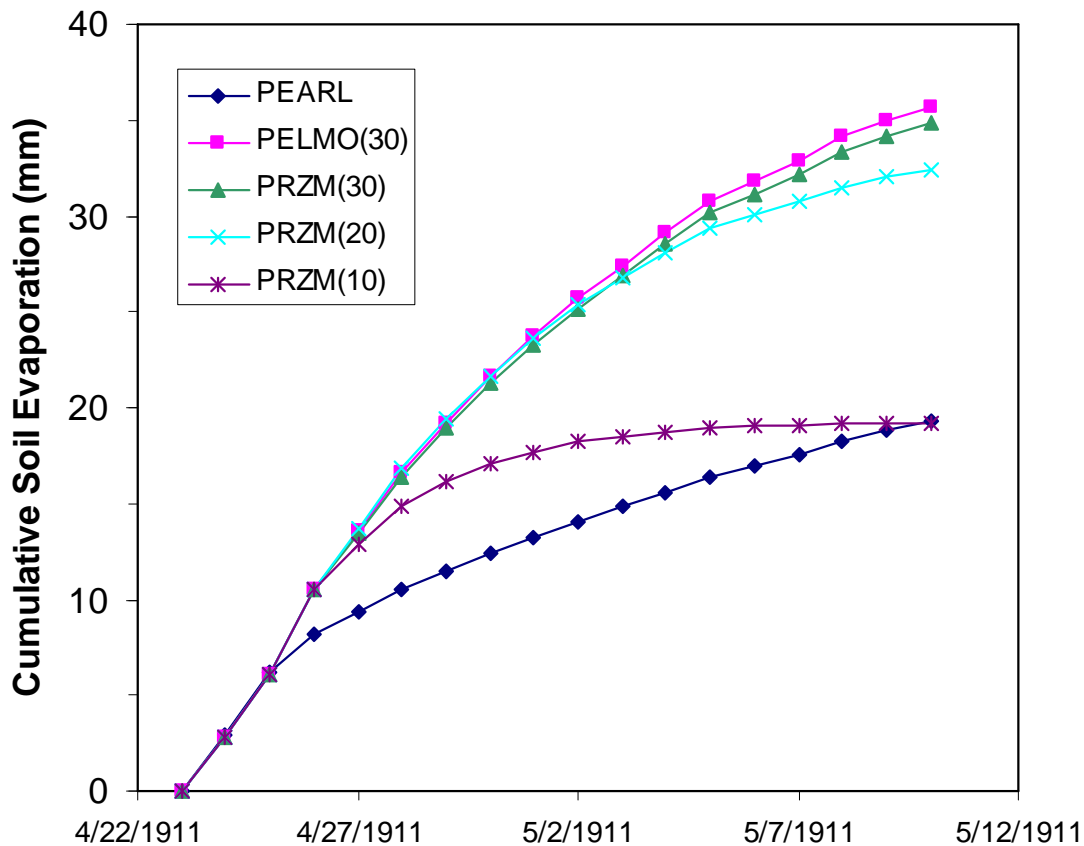
Figure 11-1. Differences in cumulative evaporation from bare soil for PEARL, PELMO, and PRZM for Thiva cabbage. Numbers is parentheses indicate the value of the ANETD parameter in cm.

The procedure used in PEARL, based on Boesten and Stroosnijder (1986), limits the amount of evaporation from the soil, based on the assumption of a specified relationship between cumulative actual evaporation and cumulative potential evaporation during a drying cycle. In bare soils with PRZM and PELMO, evaporation continues until the moisture in a specified depth of soil reaches the wilting point. The depth of soil evaporation is specified by the ANETD parameter. ANETD usually ranges between 10 and 35 cm, with higher values of ANETD used for warmer climates (Suárez, 2006). The ANETD had been set at 30 cm in the FOCUS (2000) scenarios for Sevilla and Thiva and 25 cm for Piacenza. The effect of ANETD is shown in Figure 11-1. By the end of the period essentially all of available moisture has been removed from the upper 10 cm of soil for the PRZM (10) line. While at this point the cumulative evaporation is similar for PEARL, if the dry period had continued, then evaporation would have continued in the PEARL model but not in the PRZM model with ANETD equal to 10 cm. At the end of the period the low amount of moisture left in the soil has just started to decrease the evaporation for PRZM with an ANETD equal to 20 cm.

The work group decided after reviewing the work of Torres et al. (2006) that in the absence of a crop, the routines in PEARL will be used as the standard for estimated evaporation from bare soil and the ANETD parameter in PELMO and PRZM will be adjusted to give approximately the same amount of soil evaporation during the time the crop is not present. Based on the results of this calibration procedure (presented in Appendix 21), the work group decided to use ANETD values of 15 cm for Piacenza and Sevilla and 20 cm for Thiva.

When a crop is present the different model routines still have the possibility to cause differences in the amount of evapotranspiration. PELMO and PRZM extract the potential crop evapotranspiration from the root zone, until the available water is exhausted. PEARL divides the potential evapotranspiration into soil evaporation and plant transpiration and the soil evaporation losses are described by the same routines as when there is no crop present. However, differences between the models when a crop is present appear to be much less than for bare soil.

11.5.1.4 Adjustment of the rooting depths of some crops

Because transpiration in PEARL is reduced when a substantial fraction of the roots are located below the water table, the maximum rooting depths were set at 1 m for crop/location combinations where this occurred in FOCUS (2000) or was likely to occur. These were vines at Hamburg; apples at Jokioinen; apples sugar beets, winter cereals, maize, vines, and oilseed rape at Kremsmünster, apples, citrus, and vines at Piacenza, and apples, citrus, and vines at Porto. Because of the inconsistency of evaluating ground water concentrations at a depth shallower than the root zone, the work group decided that the maximum rooting depth would not exceed 1 m for all remaining location/crop combinations.

11.5.2 Review of procedure to estimate runoff

One of the major differences in the water balance between the PEARL and the PELMO and PRZM models in the original scenarios is the amount of runoff predicted. Part of this difference was the result of runoff from irrigation (which had been originally input into PRZM and PELMO as additional rainfall). Both PRZM and PELMO will be modified so that irrigation is provided as a separate input parameter from rainfall. However, this change is still not enough to adequately harmonize the water balance between the two models (as shown in Table 11-1). In another set of simulations, different storm lengths were evaluated in PEARL to see if runoff values could be harmonised using a storm length other than 24 hours in PEARL. While the numbers in PEARL and PRZM become closer (Table 11-1), there is no reliable source of European data to determine which of the predictions is closer to reality.

Table 11-1. Comparison of runoff values estimated by PEARL (SWAP) and PELMO using the FOCUS (2000) scenarios.

FOCUS Scenario	Annual average runoff of the 20 years (mm/year) calculated with					Average annual rainfall (mm)
	SWAP 207d for rainfall intensities averaged over periods of				PELMO (no runoff from irrigation)	
	1 h	2 h	4 h	24 h		
Châteaudun; winter cereals	0	0	0	0	31	648
Hamburg; winter cereals	0	0	0	0	25	786
Jokioinen; winter cereals	43	26	12	0	52	650
Kremsmünster; winter cereals	181	102	37	5	100	899
Okehampton; winter cereals	99	24	2	0	89	1038
Piacenza; winter cereals	141	51	10	0	52	857
Porto; winter cereals	279	140	83	55	173	1150
Sevilla; winter cereals	66	29	6	0	101	493
Sevilla; potatoes	70	30	6	0	157	493
Thiva; winter cereals	61	21	2˙	0	66	500

The work group explored the use of the PESERA runoff data base for establishing benchmark runoff amounts. In the PESERA data set (Kirby et al., 2004), runoff amounts were provided for generic arable land use classes but not for the different crops used in the FOCUS scenarios. Since quite significant differences in runoff are obtained for the different crops in the FOCUS scenarios, the work group considered it necessary to rescale runoff data given for arable land-use class in the PESERA runoff map to the different crops used in the FOCUS scenarios. However, the work group could not obtain the necessary information about the procedures that were used in PESERA to calculate runoff so that this rescaling could not be carried out. Therefore, the work group decided not to use the PESERA runoff data for establishing benchmark runoff amounts for the Tier 1 scenarios.

The work group was unable to obtain a set of European-wide data to use as a reference for setting runoff amounts that would correspond to an agreed upon percentile for all soils in each FOCUS climate zone. A map of runoff estimates for Europe is under development in the EU FOOTPRINT project, but this information will not be available for use until the end of 2008, too late for use by this FOCUS work group. Therefore, due to the lack of a European-wide data set, the work group decided to make the conservative assumption of no runoff in PELMO and PRZM and to use the 24 hour storm duration for PEARL in the Tier 1 simulations. Runoff should be included in Tiers 2b and 3 when possible in EU evaluations and in simulations at the member state level when information on runoff amounts is available.

When the runoff information from the FOOTPRINT project is available, a detailed review of the data may lead to the conclusion that this could serve as a suitable data base for determining appropriate amounts of runoff in the Tier 1 scenarios. However, such a review is beyond the scope of this work group.

The work group felt that the 20[th] percentile runoff value in a FOCUS climate zone was an appropriate benchmark for runoff in the current and proposed FOCUS scenarios. However, when new scenarios are developed in the future or higher tier modelling is performed, properties determining runoff potential (such as soil hydrologic group) should be considered in a similar manner as other important soil properties such as organic matter and soil hydraulic properties in order to obtain an 80[th] percentile soil.

11.5.3 Review of estimation of the irrigated amounts of water

In the FOCUS (2000) scenarios irrigation schedules were developed for groups of crops rather than individual crops. A review of the irrigation schedules for the FOCUS (2000) scenarios showed that the irrigation and the cropping periods did not always match. Also in some cases the amounts appeared to be higher than were actually applied, based on local information. During the work on harmonising the water balance, the work group also discovered that water stress occurred to some crops in the FOCUS (2000) Porto scenarios, which does not assume irrigation; whereas irrigation is usually applied. The irrigation information collected by the work group is summarized in Appendix 22.

The work group decided that irrigation schedules should be developed for individual crops in Châteaudun, Piacenza, Porto, Seville, and Thiva. These irrigation schedules provide irrigation from the time of planting until start of senescence and are generated using irrigation routines in PEARL and PELMO, which apply irrigation once a week on a fixed day to bring the root zone up to field capacity. However, irrigation was applied only if the amount required exceeded 15 mm. Because of the minor differences remaining in the water balance (primarily evapotranspiration), the irrigation routines for PEARL and PELMO predict somewhat different amounts. However, using different irrigation routines tends to compensate for evapotranspiration differences to provide closer estimates between the two models for the amount of water moving below the root zone, which is the key water balance parameter affecting leaching. The irrigation amounts generated by PELMO are used directly in PRZM. While allowing PRZM to generate irrigation amounts is also possible, the work group decided that this added a level of complexity that was not needed, given the similarity of PELMO and PRZM.

The amounts of irrigation for each of the location/crop combinations are presented in the examples shown in Chapter 12 and Appendix 23.

11.6 Soil pH values in FOCUS scenarios

The soil pH values at various depths for the FOCUS ground water scenarios were available in the FOCUS ground water documentation but were not made available electronically for use with models.   This meant that substances showing a correlation between adsorption and soil pH had to be modelled using an experimental adsorption value appropriate to the soil pH of each relevant FOCUS scenario.

This FOCUS ground water group have decided to make the pH-H_2O values of the FOCUS groundwater scenarios available electronically because most of the values provided for the soil profiles were pH-H_2O values (FOCUS, 2000). Models may now be used to describe the sorption of substances showing pH dependent sorption, however the modelling report should demonstrate that the adsorption values predicted by the model fit the experimental data. Using an experimental adsorption value appropriate for the soil pH of the relevant FOCUS scenario is still an acceptable method of including pH dependent sorption into the FOCUS scenarios. However, as stated in Section 11.1, this does not imply that these scenarios can necessarily be considered to possess the FOCUS-defined vulnerability regarding pH effects.

When introducing a measured K_{oc}-pH relationship into the FOCUS leaching models, the pH-H_2O measuring method must be consistent with that used for analysing the sorption measurements. If the pH-H_2O is not available for the soils from the adsorption studies, it can be calculated as follows (A.M.A. van der Linden, personal communication, 2008):

pH-H_2O = 0.820 pH-KCl + 1.69

pH-H_2O = 0.953 pH-$CaCl_2$ + 0.85

where pH-KCl is the pH measured in an aqueous solution of 1 mol/L of KCl and where pH-$CaCl_2$ is the pH measured in an aqueous solution of 0.01 mol/L of $CaCl_2$.

11.7 Review of procedure for estimating interception of pesticide by plants

When FOCUS (2000) decided to estimate interception of pesticide application by the plant canopy using experimental measurements available in the literature, not all of the FOCUS

models contained a routine for estimating crop interception. Since all the models recommended by FOCUS for estimating ground water concentrations can now estimate interception; the work group reviewed whether the Tier I recommendations be changed to allow them to do so (Appendix 24). At this time the work group decided not to change this recommendation.

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12 COMPARISON OF CURRENT AND REVISED SCENARIOS

One of the objectives of the revisions described in Chapter 11 was to standardise the assumptions used by the FOCUS models to reduce the variability of predictions among models. This objective was largely addressed by the harmonisation of dispersion length and the water balance. Other revisions resulted in changes not directed towards harmonisation of model predictions. This included the change in the 80[th] percentile weather concentration to the average of the 16 and 17[th] ranked values (reducing concentrations for all scenarios at least slightly), the change in the Porto soil profile (increasing concentrations for all crops grown in Porto), and the change in the Piacenza soil profile (lowering concentrations for all crops grown in Piacenza). This chapter compares the proposed ground water scenarios with the current ground water scenarios of FOCUS (2000) as amended by the actions of the FOCUS Version Control Work Group to date. This chapter does not consider the effects of the various individual changes, but only the changes as a whole.

12.1 Results of comparison simulations

A comparison of the changes was performed by conducting simulations with pesticide D (as defined by FOCUS, 2000) for all 125 location/crop combinations and for the proposed revision of these 125 location/crop combinations as described in this report. A single application at 1 kg ai/ha was assumed to occur the day before plant emergence. For those location/crop combinations with two cropping periods, single applications of 1 kg ai/ha were made during each of the cropping periods. For apples, citrus, grass, and vines, the applications was assumed to occur on May 1. As outlined by FOCUS (2000), simulations for each location/crop combination were performed for a 26 year period (6 year warm-up period followed by 20 year simulation period). Water balance components were calculated as the average of the 20 year annual values and PECgw was calculated for the current scenarios as outlined by FOCUS (2000) and for the proposed scenarios as outlined in Section 11.2. This chapter focuses on the changes occurring with PEARL and PELMO, since the predictions of PRZM are similar to PELMO. However, detailed information on the results of these simulations is presented for all models in Appendix 23 (Information on MACRO will be included as soon as it is available). The work group also intends to make the information in Appendix 23 available in a spreadsheet to be posted on the FOCUS web site, once the report has been approved, to facilitate comparisons.

As part of the checking process, significant differences among model predictions were found when 1/n values of 0.7 were used. The work group is exploring the reason for these differences and solutions will be proposed prior to the release of the scenarios on the FOCUS web site.

The variability between PEARL and PELMO in the current scenarios (hereafter referred to as FOCUS 2000) is shown in Figure 12-1 for PECgw at one meter and in Figure 12-2 for the percolation of water past 1 m. Figures 12-3 and 12-4 present the same comparisons for the proposed scenarios (hereafter referred to as FOCUS 2009).
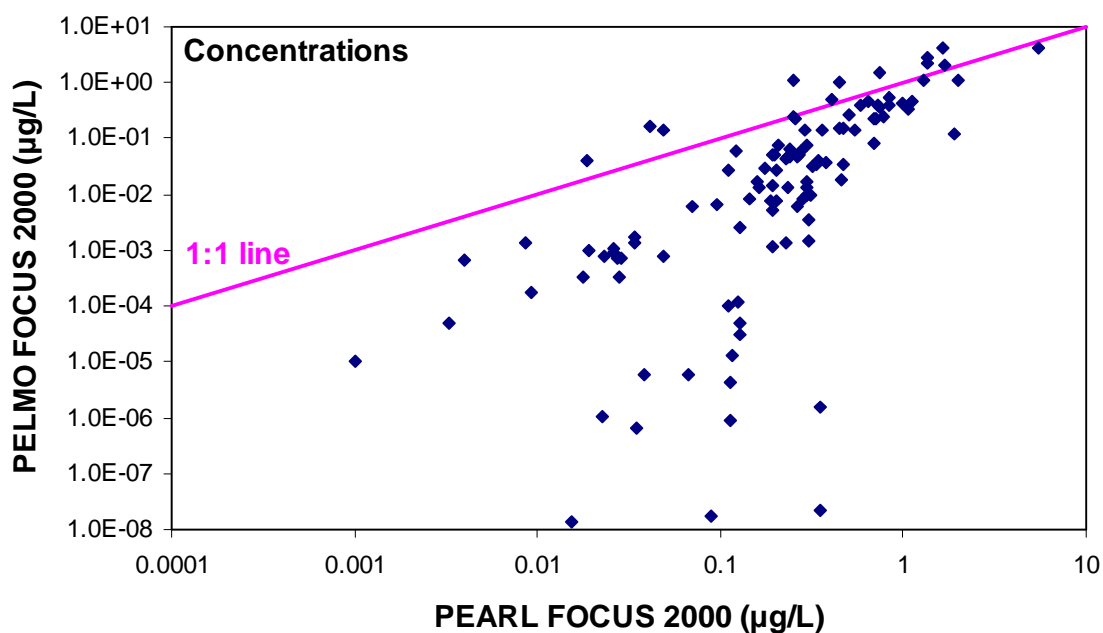
Figure 12-1. Comparison of PECgw predicted by PEARL and PELMO for all 125 FOCUS 2000 scenarios.
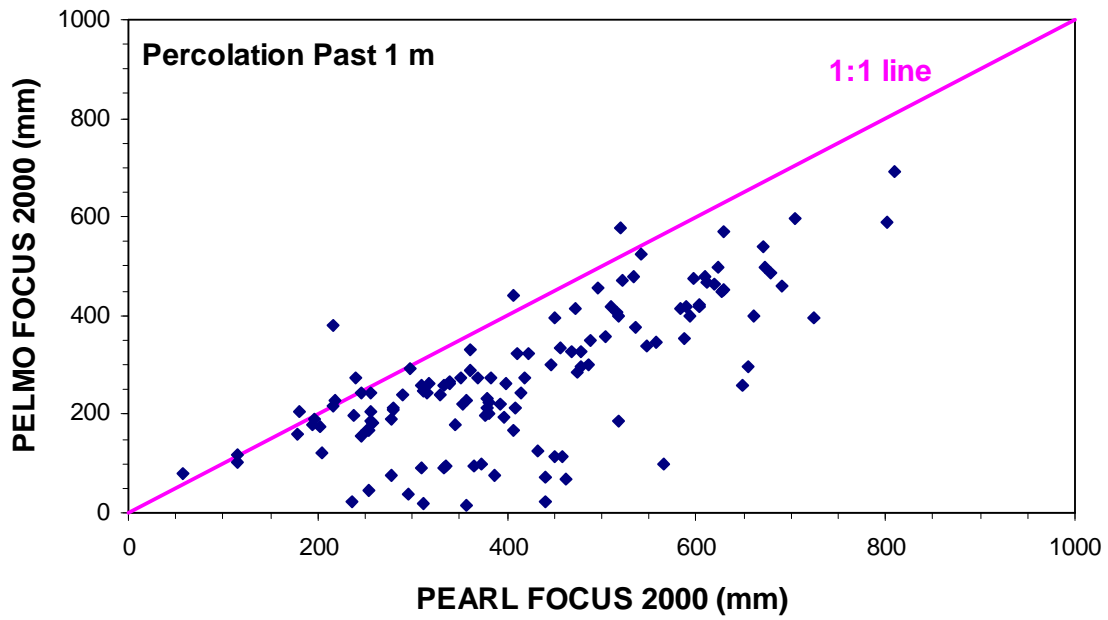
Figure 12-2. Comparison of the percolation past 1 m predicted by PEARL and PELMO for all 125 FOCUS 2000 scenarios. Values are the average of the 20 annual values.
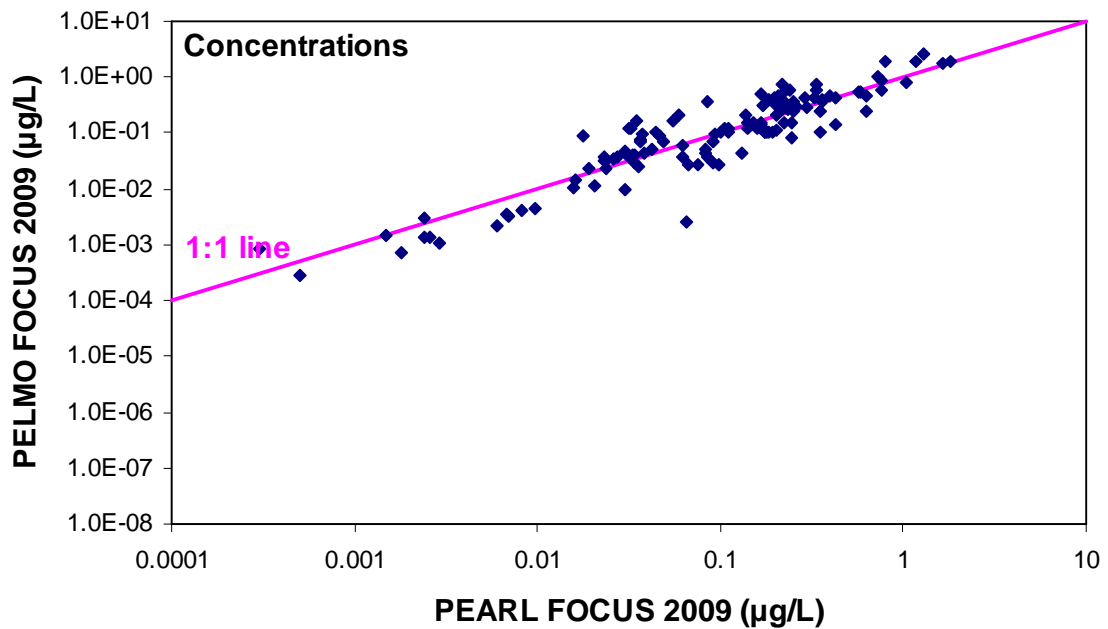
Figure 12-3. Comparison of PECgw predicted by PEARL and PELMO for all 125 FOCUS 2009 scenarios.
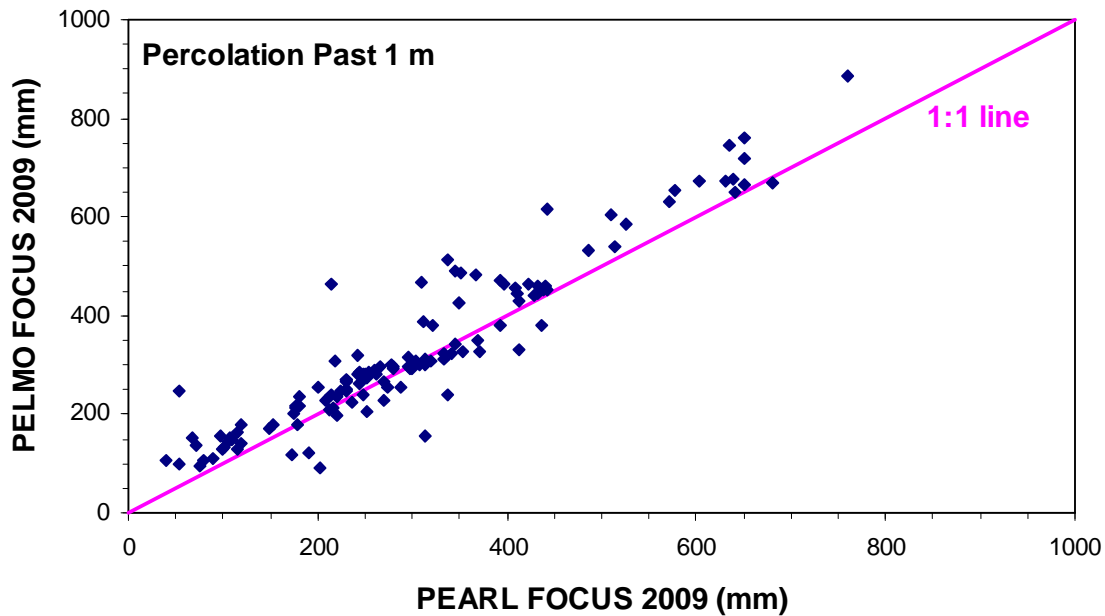
Figure 12-4. Comparison of the percolation past 1 m predicted by PEARL and PELMO for all 125 FOCUS 2009 scenarios. Values are the average of the 20 annual values.

Figure 12-1 shows that with FOCUS 2000 scenarios the predictions of PECgw by PEARL are generally higher than those predicted by PELMO and that the percolation past 1 m was also generally higher for PEARL (Figure 12-2). With the FOCUS 2009 scenarios, overall the concentrations predicted by PEARL essentially the same (as the concentrations predicted by PELMO (Figure 12-3), with the concentrations predicted by PELMO on average slightly higher than predicted by PEARL. The agreement between concentrations is also better with only about 10 percent of the PEARL 2009 and PELMO 2009 values greater than a factor of 3 different. This compares to 76 percent being greater than a factor of 3 apart in the FOCUS 2000 scenarios. The agreement between percolation amounts also has been significantly improved in the FOCUS 2009 scenarios. With FOCUS 2009 scenarios, PELMO generally predicts more percolation past 1 m compared to PEARL (Figure12-4), and the reverse is true with the FOCUS 2000 scenarios (Figure 12-2).

The comparison of PECgw between PRZM and PELMO and between PRZM and PEARL is presented in Figures 12-5 and 12-6, respectively, for the FOCUS 2009 scenarios. Overall, PRZM tends to predict somewhat lower concentrations than PELMO and PEARL although agreement among the three models remains satisfactory (the difference between PEARL and PRZM predictions is most evident at lower concentrations, the overall average, which is controlled by the scenarios with higher concentrations is essentially the same for both

models). The difference in the concentrations between PRZM and PELMO with the FOCUS 2009 scenarios is somewhat surprising given the good agreement between the two models for percolation past 1 m (Figure 12-7). However, this difference in concentrations was also present (and slightly larger) in the FOCUS 2000 scenarios (Figure 12-8) so the concentration difference is not a function of the way dispersion was implemented in the two models (both models use exactly the same code). The precise reason for the difference between PELMO and PRZM is not known but presumably is caused as a result of the small differences in the way ET is extracted from the soil (PRZM tends to remove ET closer to the surface), differences in the way the surface of the soil is represented in the two models, and/or differences in the thickness of the depth increments in the soil profile (PRZM uses 1 mm increments in the upper 10 cm of soil while PELMO uses 1, 2.5, and 5 cm increments for the horizon corresponding to the three default degradation zones generally the upper 30 cm, 30 to 60 cm, and below 60 cm, respectively). Part of the differences between PRZM and PELMO in the FOCUS 2000 scenarios was due to the differences in the way degradation was handled below 0°C, but the FOCUS 2009 version of PRZM uses the assumptions in PEARL and PELMO. In the FOCUS 2009 scenarios, the most systematic differences occurred in the Thiva scenarios where degradation rates at low temperatures is not a relevant factor.
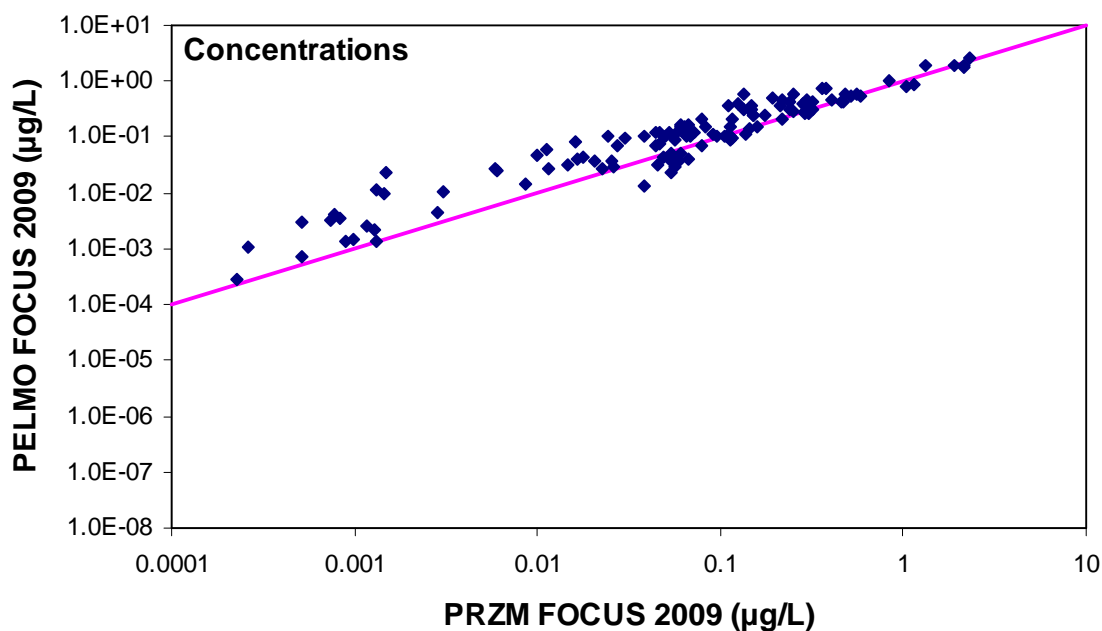
Figure 12-5. Comparison of PECgw predicted by PRZM and PELMO for all 125 FOCUS 2009 scenarios.
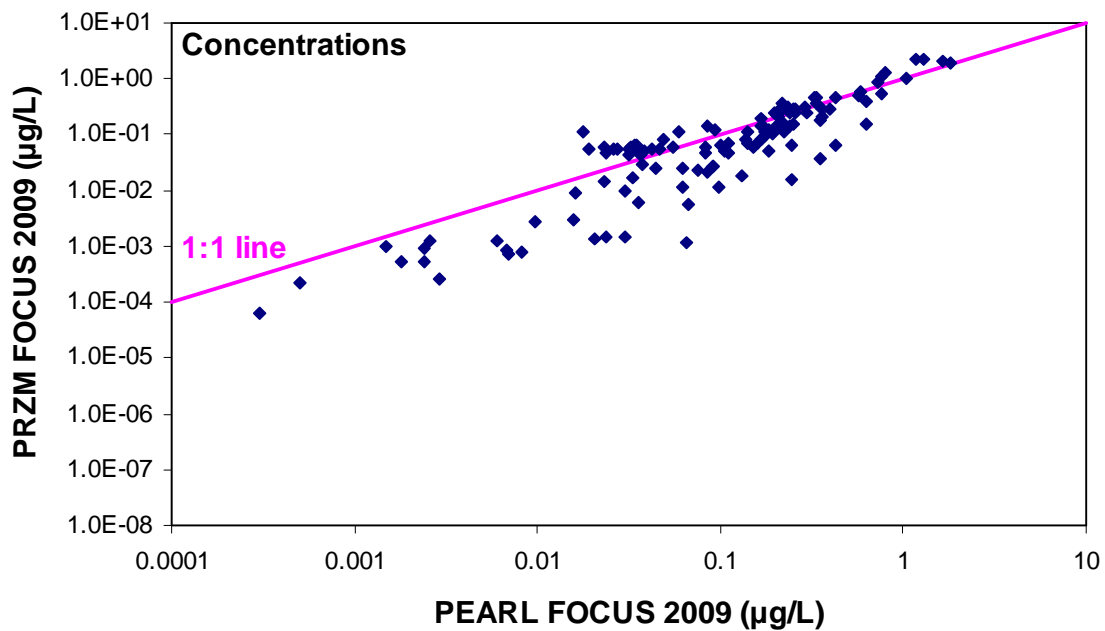
Figure 12-6. Comparison of PECgw predicted by PRZM and PEARL for all 125 FOCUS 2009 scenarios.
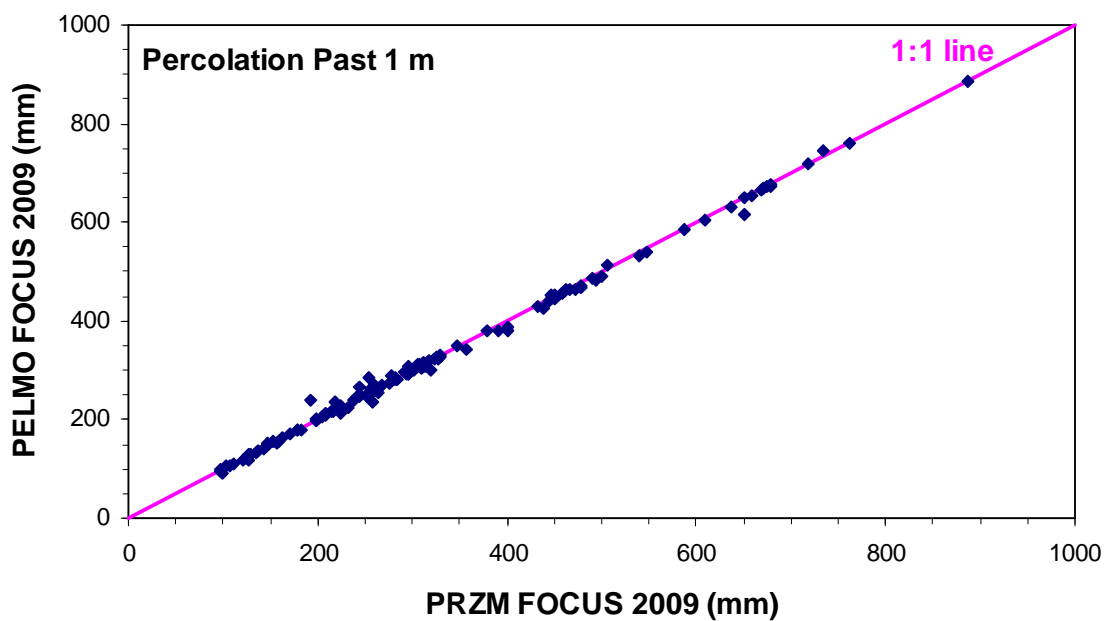
Figure 12-7. Comparison of the percolation past 1 m predicted by PRZM and PELMO for all 125 FOCUS 2009 scenarios. Values are the average of the 20 annual values.
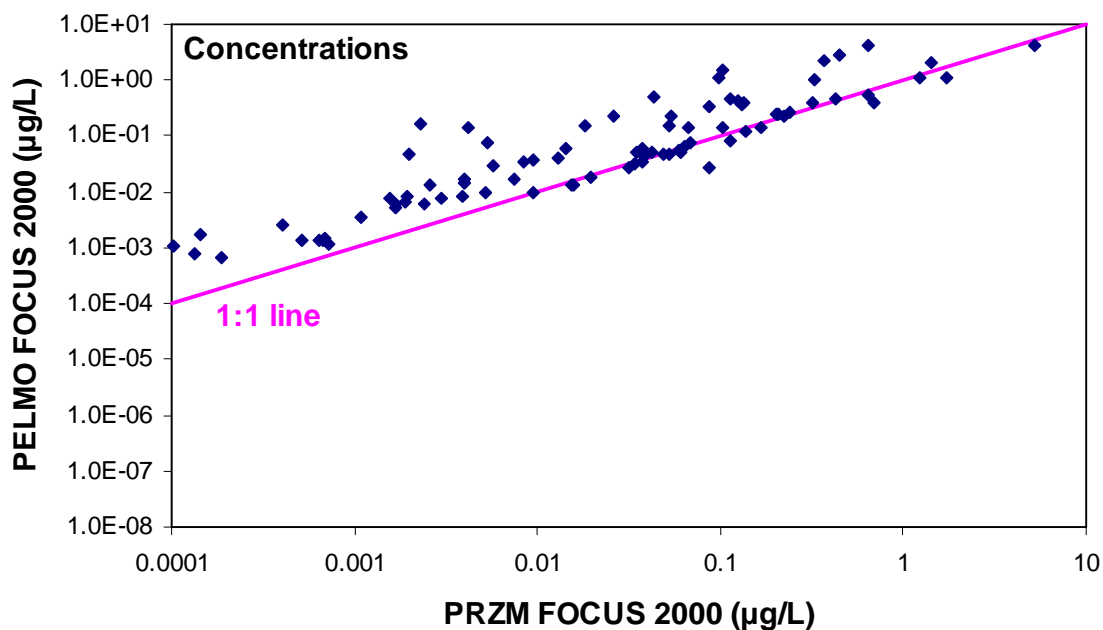
Figure 12-8. Comparison of PECgw predicted by PRZM and PELMO for all 125 FOCUS 2000 scenarios.

As shown in Figure 12-9, PECgw values predicted by PEARL with the FOCUS 2009 scenarios are generally lower than with the FOCUS 2000 scenarios. Conversely, the concentrations predicted by PELMO and PRZM with the FOCUS 2009 scenarios are generally higher than with the FOCUS 2000 scenarios (Figures 12-10 and 12-11). The major exceptions to the general reduction in concentrations predicted by PEARL with the FOCUS 2009 scenarios are the two points in the upper left-hand corner of Figure 12-9. These two points represent winter rape and winter cereals in Porto and the higher concentrations are due to the change in the soil profile.
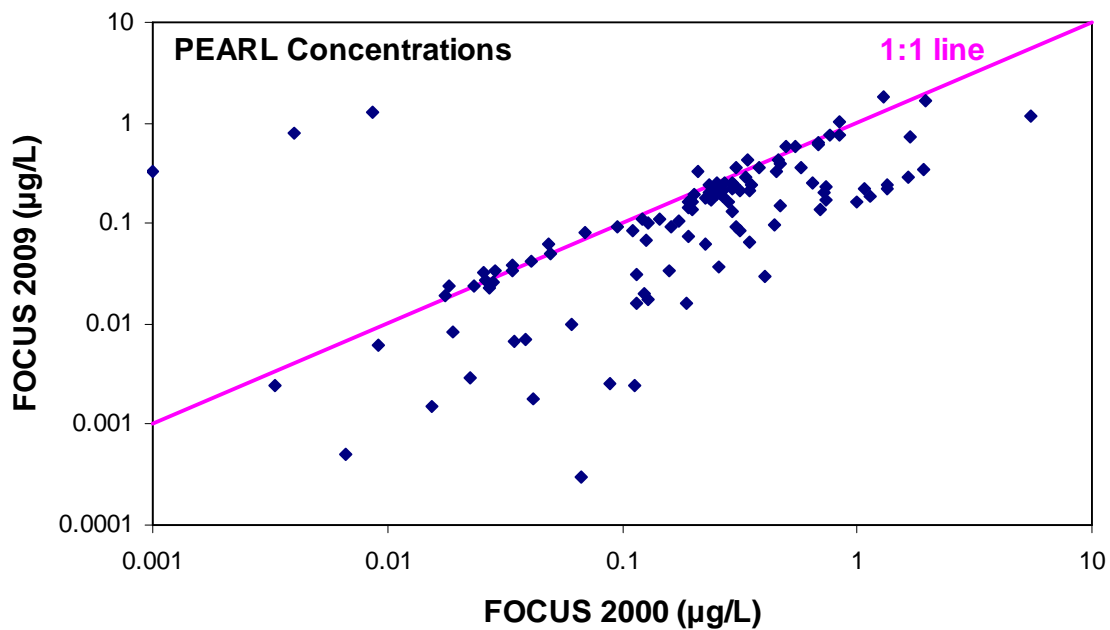
Figure 12-9. Comparison of PECgw predicted by PEARL for all 125 FOCUS 2000 and FOCUS 2009 scenarios.
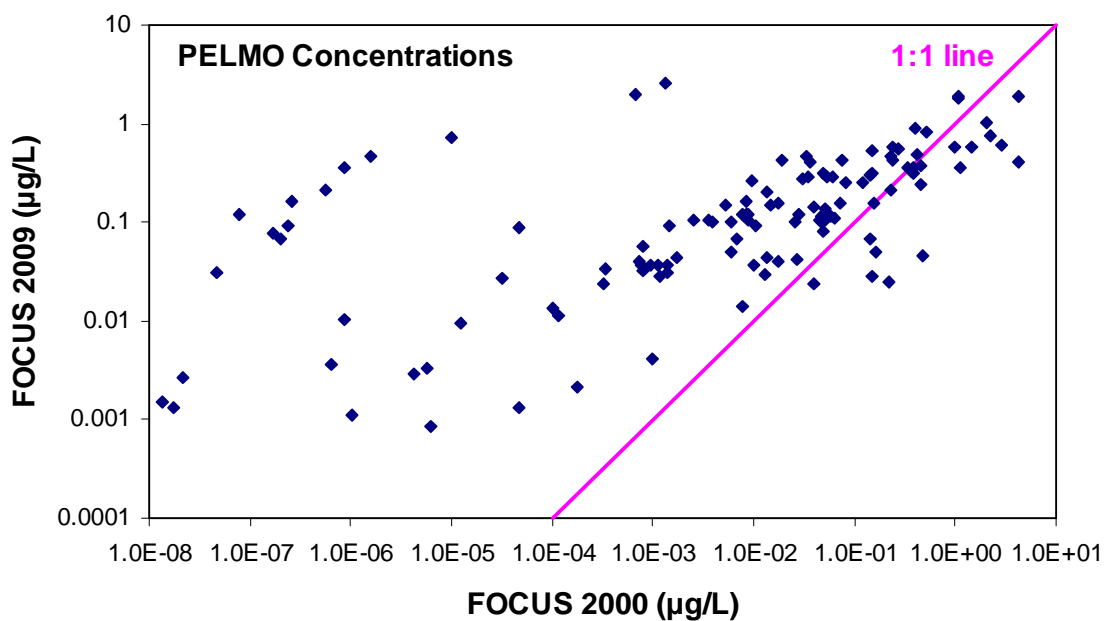
Figure 12-10. Comparison of PECgw predicted by PELMO for all 125 FOCUS 2000 and FOCUS 2009 scenarios.
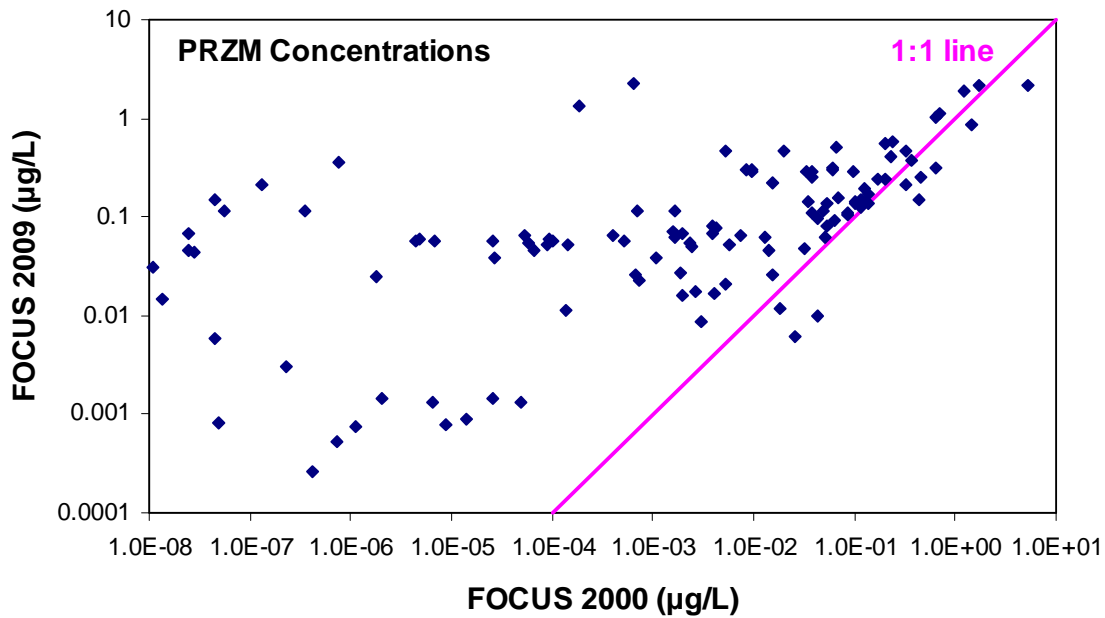
Figure 12-11. Comparison of PECgw predicted by PRZM for all 125 FOCUS 2000 and FOCUS 2009 scenarios.

As shown in Figure 12-12, the amount of percolation past one meter predicted by PEARL is generally lower in the FOCUS 2009 scenarios than in the FOCUS 2000 scenarios primarily due to the decreased irrigation amounts (as discussed later in this section) and increased reference evapotranspiration. PELMO did not show this decrease because eliminating runoff offset the increasing reference evapotranspiration reductions and as a result there was no overall decrease in irrigation. The amount of percolate with PELMO and PRZM generally is a little higher in the FOCUS 2009 scenarios than in the FOCUS 2000 scenarios (Figures 12-13 and 12-14).
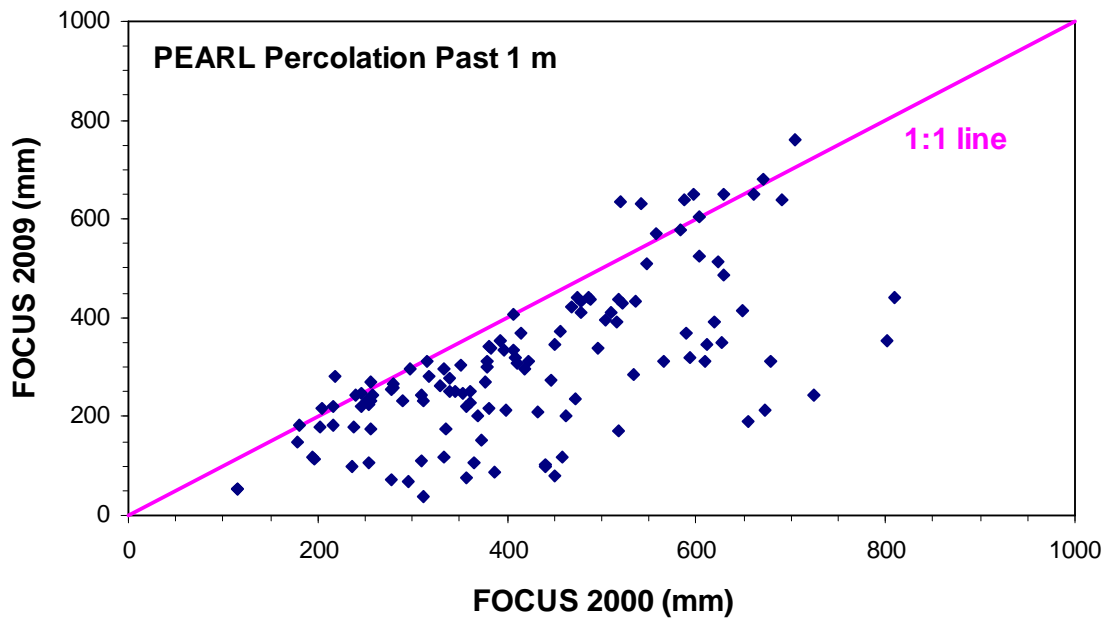
Figure 12-12. Comparison of the percolation past 1 m predicted by PEARL for all 125 FOCUS 2000 and FOCUS 2009 scenarios. Values are the average of the 20 annual values.
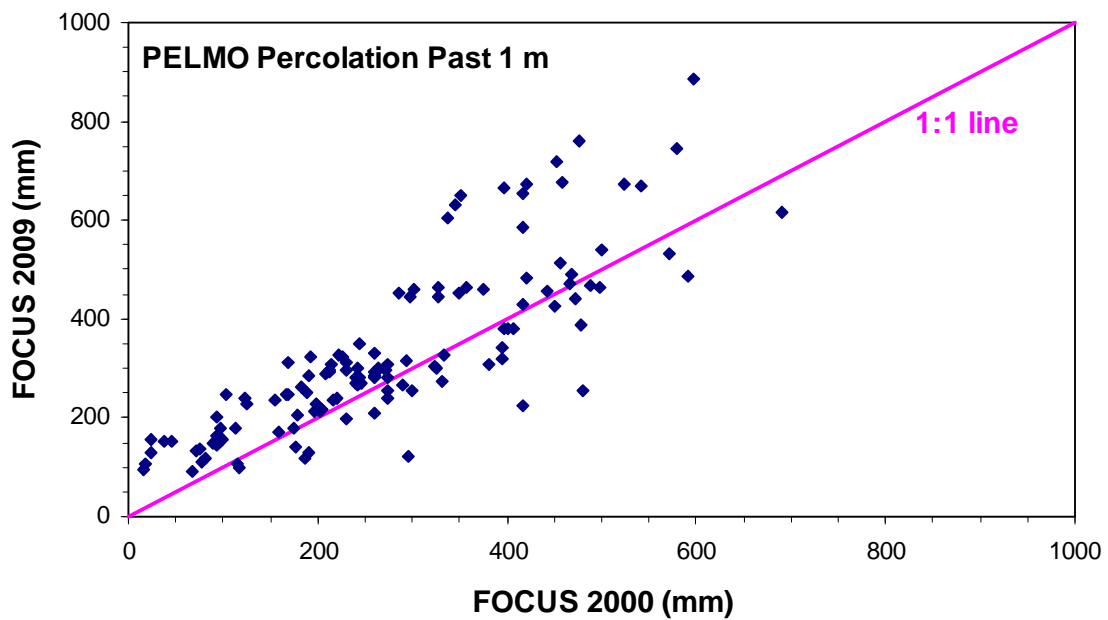
Figure 12-13. Comparison of the percolation past 1 m predicted by PELMO for all 125 FOCUS 2000 and FOCUS 2009 scenarios. Values are the average of the 20 annual values.
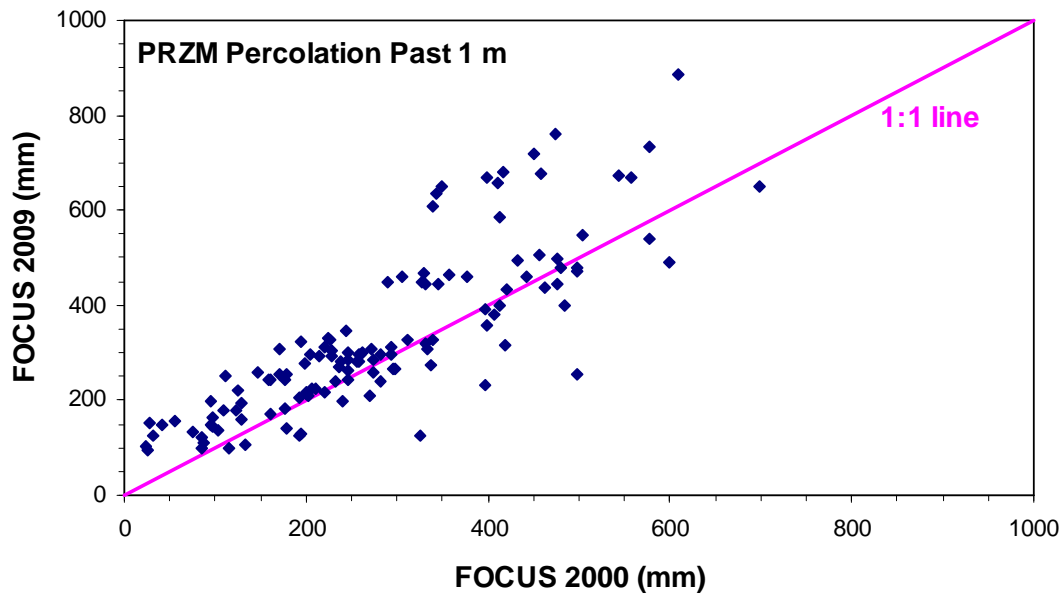
Figure 12-14. Comparison of the percolation past 1 m predicted by PRZM for all 125 FOCUS 2000 and FOCUS 2009 scenarios. Values are the average of the 20 annual values.

The analysis of the comparison simulations also included various components of the water balance. Figures 12-15 through 12-17 show a comparison of the values for potential evapotranspiration, actual evapotranspiration, and irrigation, respectively, calculated by PEARL and PELMO for the FOCUS 2009 scenarios.
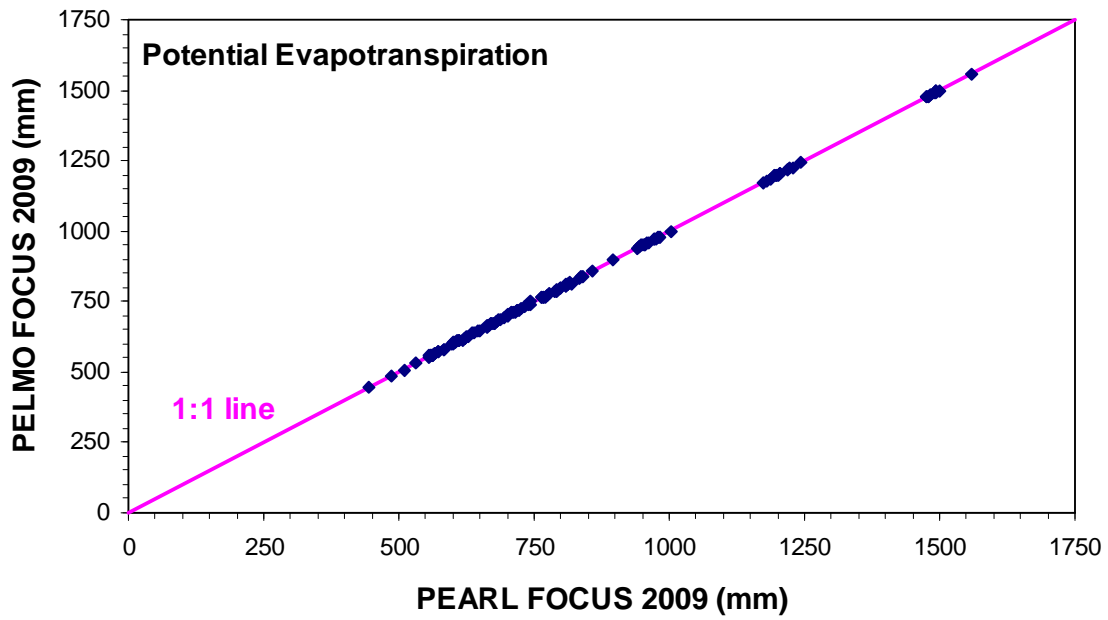
Figure 12-15. Comparison of the potential evapotranspiration predicted by PEARL and PELMO for all 125 FOCUS 2009 scenarios.
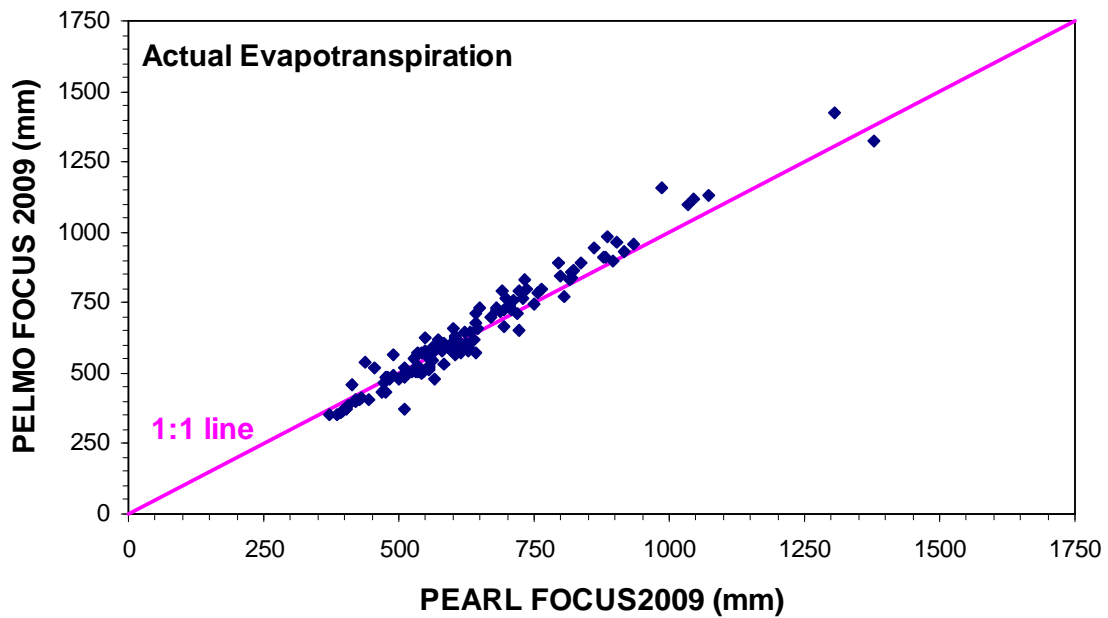
Figure 12-16. Comparison of the actual evapotranspiration predicted by PEARL and PELMO for all 125 FOCUS 2009 scenarios. Values are the average of the 20 annual values.
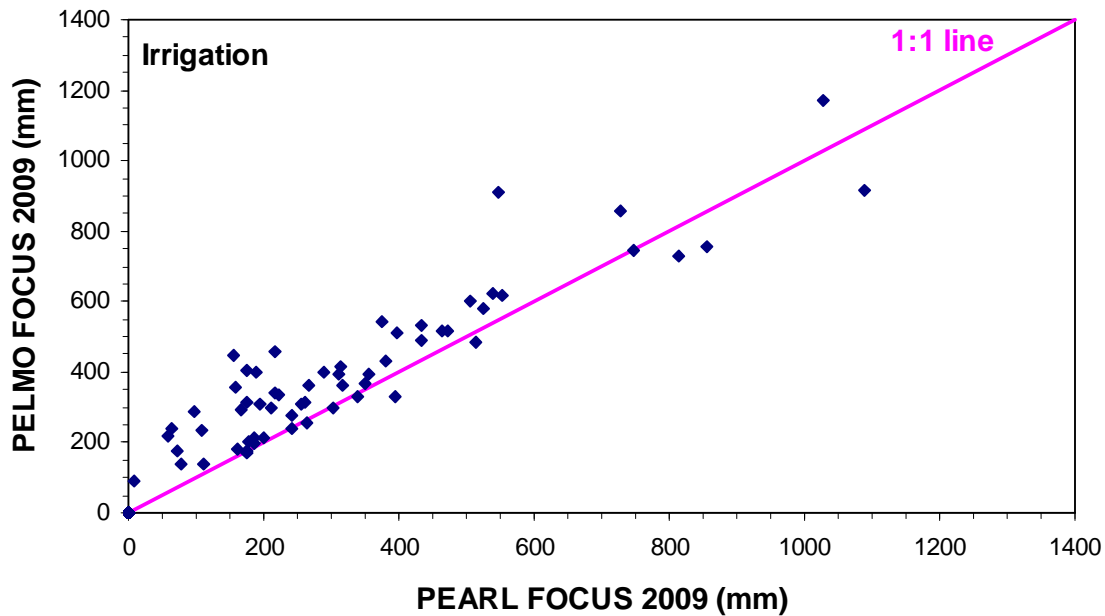
Figure 12-17. Comparison of the irrigation generated by PEARL and PELMO for all 125 FOCUS 2009 scenarios. Values are the average of the 20 annual values.

Potential evapotranspiration is calculated in the models by multiplying the reference evapotranspiration data in the weather data file by the crop coefficient and since these values are the same for all models the predicted values should also be similar among all of the models. The small differences shown in Figure 12-15 are probably due to the different handling of leap years by the models and other subtle differences in the procedures to calculate daily potential evapotranspiration.

Figure 12-16 shows relatively good correlation between the actual evapotranspiration predicted by PEARL and PELMO. The amount of actual evapotranspiration predicted by PELMO would generally be expected to be somewhat higher since the evapotranspiration in PEARL is divided into soil evaporation and plant transpiration and the evaporation from the soil surface is limited after several days of no rainfall. PELMO and PRZM do not split evapotranspiration when plants are present so that all of the potential evapotranspiration is available for actual evapotranspiration, even in periods of low rainfall.

The effect of the different evapotranspiration routines is offset in some scenarios by the effect of capillary rise in locations with shallow water tables, especially in Piacenza. This process is included in PEARL but not in PELMO or PRZM. Calculations indicate that the effect of

capillary rise adds an upward flux of 150-200 mm per year in Piacenza, depending on the specific crop. In Porto, the effect is much less (15-45 mm per year).

In general the irrigation generated by PELMO for the FOCUS 2009 scenarios is higher than predicted by PEARL (Figure 12-17). Capillary rise, upward movement of water in the soil profile, and limitations on soil evaporation when a plant is present are all factors contributing to the lower irrigation amounts predicted by PEARL. Overall the amounts of irrigation generated by PEARL with the FOCUS 2009 scenarios were somewhat less than the amounts of irrigation in the FOCUS 2000 scenarios (Figure 12-18) (not considering the additional Porto scenarios, which are located on the y-axis). Overall, the amounts of irrigation generated by PELMO for the FOCUS 2009 scenarios (these were also the irrigation amounts used by PRZM) were similar to the amounts of irrigation in the FOCUS 2009 scenarios (not considering the additional Porto scenarios), except that there is considerable variation for individual scenarios (Figure 12-19).
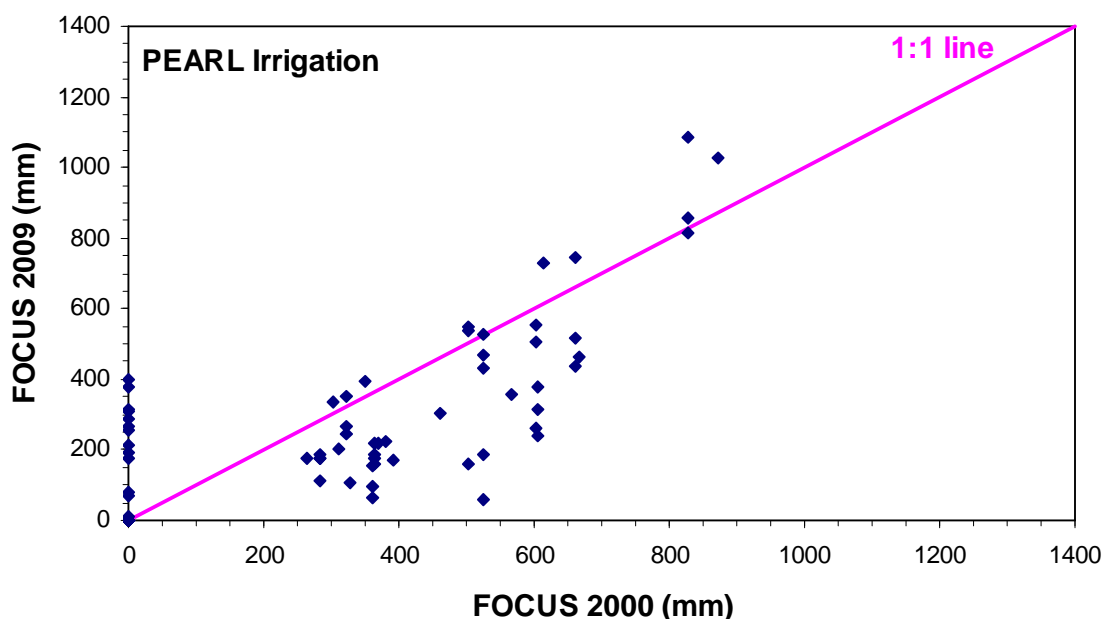
Figure 12-18. Comparison of the irrigation generated by PEARL for all 125 FOCUS 2009 scenarios with those used in the FOCUS 2000 scenarios. Values are the average of the 20 annual values.
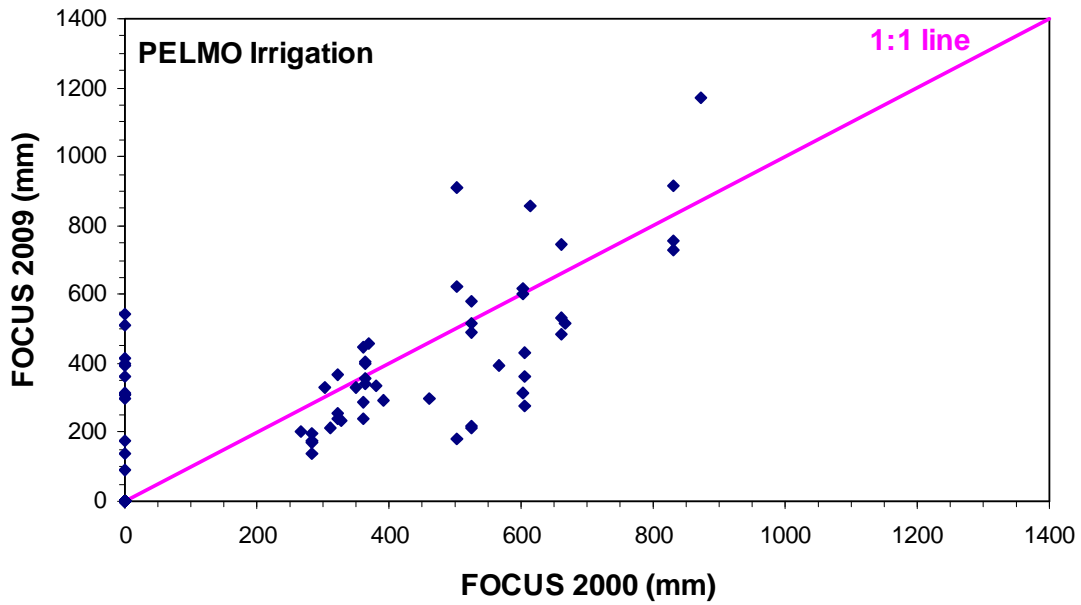
Figure 12-19. Comparison of the irrigation generated by PELMO for all 125 FOCUS 2009 scenarios with those used in the FOCUS 2000 scenarios. Values are the average of the 20 annual values.

Even more important than the changes in irrigation amounts were the changes in irrigation timing. In the FOCUS 2000 scenarios the cropping dates (emergence, maturity, and harvest) used to generate the irrigation schedules were not necessary the cropping dates used in the scenarios, so in some cases irrigation was applied when no crop was present. The generation of the irrigation schedules in the FOCUS 2009 scenarios by PEARL and PELMO resulted in matching the cropping dates as well as accounting for the rainfall patterns more precisely (irrigation events were eliminated in the irrigation schedules in the FOCUS 2000 scenarios when significant rainfall had occurred).

12.2 Conclusion

The harmonisation effort was largely successful with 90 percent of the PEARL and PELMO values for the proposed scenarios within a factor of three. This compares to less than one-fourth of the current scenarios. Given the current agreement among the models, the work group recommends that the ground water assessments can now be performed with any of the models (PEARL, PELMO, and PRZM) and there is no need to perform the assessments with more than one model.

12.3 References

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2, 202pp.

13 APPLICABILITY OF FOCUS GROUND WATER SCENARIOS TO THE NEW MEMBER STATES

13.1 Introduction

13.1.1 Objective of this study

In 2000 the first FOCUS groundwater group defined a set of 125 leaching scenarios that represent collectively major agricultural areas in the EU before May 1, 2004. The general approach for establishing the scenarios was to select locations in major agricultural areas that covered the diversity of EU agriculture (FOCUS, 2000). With the accession of ten in additional countries in 2004 (and more recently two additional countries) the applicability of present FOCUS leaching scenarios to the extended agricultural area of the EU after 2004 must be assessed.

This chapter aims to provide a first assessment of the applicability of existing FOCUS scenarios to New Member Countries (NMC). After the selection of appropriate data layers a first classification of Europe according to the definition of FOCUS (2000) is given. Due to several limitations of this rather general classification scheme a more detailed analysis based on climate and soil properties of the existing nine locations is deemed appropriate before drawing a final conclusion about the applicability of current scenario to NMCs. This refined assessment consists of three steps:

1) Identification of spatial indicators to express the applicability of a scenario
2) Visualisation of the spatial extent of each scenario
3) Identification of missing areas

13.1.2 Limitations

The FOCUS leaching scenarios represent collectively major agricultural areas and a broad range of crops. As a consequence the scenarios do not represent a specified worst-case percentile for a particular country or pesticide. For that reason the approach presented in this chapter differs from other approaches that are outlined in Section 7.2.5 and Appendices 4 and 5 in this report.

This chapter assesses whether the existing set of FOCUS scenarios 'covers' the agricultural area of new member countries. A scenario 'covers' an area when it represents either the same properties or represents a more vulnerable situation like higher rainfall amounts or lower organic carbon contents. This chapter does not attempt to quantify the exact percentile

of vulnerability in new member states that is covered by each scenario since such a target requires crop- and compound-specific GIS methods.

13.2 Materials and methods

13.2.1 Data sources

13.2.1.1 Climate data
The result of any spatial analysis with regional climate data is affected by the nature of the underlying data. For that reason two data sets were tested with regard to their applicability in this study. Both data bases cover the area of interest to a sufficient extent and allow for conclusions on the general weather pattern. Details of the data bases are given in Appendix 8.

(A) Global climate data 1960 – 1990, Intergovernmental Panel on Climate Change, United Nations Environment Program (= IPCC, 2004)

(B) Interpolated Meteorological Data 1992 – 2002, JRC MARS Database – EU Commission, JRC (= MARS, 2004)
The MARS weather data base contains more recent weather data from approximately 1500 weather stations. Point data were interpolated to a 50 x 50 km grid and covers most of the area of the EU. All weather parameters are reported as **daily** values and originate exclusively from weather stations that are located in agricultural areas. Note that a small number of grid cells in Scandinavia and Estonia do not contain data for the entire period of 11 years.

Note that both data sets contain **interpolated** data from selected weather stations; in this way both data bases are subject to errors. Nevertheless, conclusions can be drawn about the applicability of each data base for the purpose of this assessment. The differences between both data bases and its implications for leaching assessments is summarised in Table 13-1.

Table 13-1. Differences between MARS and IPCC data

Differences between MARS and IPPC	Remarks	Implication for leaching assessments
Higher spatial variation of temperature and rainfall classes in MARS	MARS was interpolated on the basis of a greater number of weather stations than IPCC. As a consequence most weather stations were interpolated to a smaller area, resulting in sharper class boundaries.	The interpolation of temperature in MARS was done on the basis of altitude. In this way the spatial variation reflects also a changing relief and is thus more realistic. Rainfall data was not interpolated in MARS but taken directly from the stations. The large number of weather stations suggests that the variability of rainfall is captured to a better extent than in IPCC.
Minimum and maximum values in IPCC exceed those of MARS	Interpolated weather data in MARS originates only from weather stations in agricultural areas. In contrast to that IPPC data were derived from weather stations in agricultural and non-agricultural areas.	Leaching assessments have to account for realistic weather conditions in agricultural areas. MARS contains data with a bias towards agricultural areas which is of advantage for the purpose of risk assessments for pesticides.
IPCC contains 30-year monthly average data whereas MARS provides 11-year daily weather data		30-year average data is more robust than 11-year data, however this advantage of IPCC is compensated by the fact that part of the data was derived from stations in non-agricultural areas
IPCC data covers the globe; MARS is a European data base only		IPCC data allows for comparisons between climate conditions in different continents which is relevant when assessing the applicability of e.g. U.S. or Canadian field studies to Europe and vice-versa
IPCC data comprises data from 1960 – 90 whereas the available MARS data base contains data from 1992 – 2002		Whether climate change phenomena exert a significant influence on mean weather patterns is uncertain, although likely a more recent data base will be more accurate in terms of rainfall volumes and temperature

Due to the higher spatial and temporal resolution of MARS, only MARS data was used in this assessment. MARS has the inherent advantage of providing daily weather data which can be readily used for simulations with FOCUS leaching models. Note that MARS does not

provide complete weather series from 1992 – 2002 for parts of Scandinavia and Estonia. A complete coverage of the entire area of interest is given for the period 1995 – 2002, for that reason 8-year data was used for Scandinavia and 11-year data for the rest of Europe (see Figure 13-1).
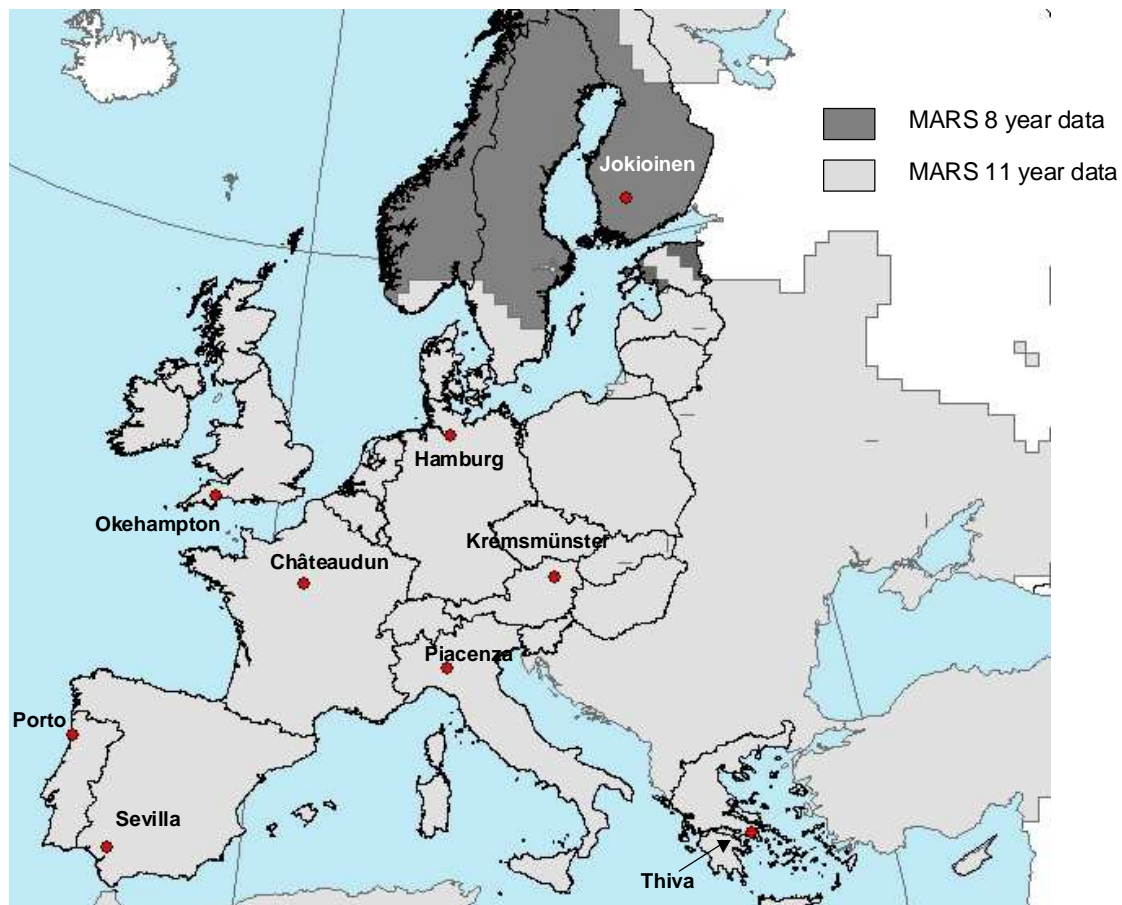
Figure 13-1. Periods covered by MARS climate data.

13.2.1.2 Soil texture

Soil texture information was taken from the EU soil map (SGDBE, 1998, see also Appendix 8) containing information about soil mapping unit (SMU) distribution in Europe and availability of soil typological units (STU) within the SMU. A new attribute table (SPADE II, release 2006) will contain more detailed profile data for STU's used as arable land. In the present version of the EU soil map only a few STU's are linked with soil profile data. For that reason the assessment was done with soil texture information at the STU level. At this level the soil texture is only available in classified form as shown in Table 13-2.

214

Table 13-2. Soil texture information at the STU level in the EU soil map.

Class	Description
1	Coarse (clay < 18 % and sand > 65 %)
2	Medium (18% < clay < 35% and sand > 15%, or clay < 18% and 15% < sand < 65%)
3	Medium fine (clay < 35 % and sand < 15 %)
4	Fine (35 % < clay < 60 %)
5	Very fine (clay > 60 %)
9	No texture (histosols, ...)

13.2.1.3 Organic carbon content in topsoil

Organic carbon contents in topsoil are provided by a raster map in 1 x 1 km resolution (Jones et al. 2004, 2005). The respective data set was derived on the basis of the EU soil map, topography, climate, and land use and is currently the most detailed data base for organic carbon contents in topsoil.

13.2.1.4 Land use

Corine Land Cover (250 x 250 m) was used to restrict the assessment on agricultural areas. Corine Land Cover is based on remote sensing data and covers the entire area of interest except Sweden and Cyprus (at the time the map was made, Corine did not cover Sweden and Cyprus, but currently covers all of the European Union).

After climate and soil parameters, the distribution of arable land must be considered. In this general assessment, the spatial distribution of individual field crops was neglected, resulting in arable land being considered as a whole. The respective data was taken from Corine Land Cover. However additional information on the distribution of individual field crops should be considered when assessing how representative a specific cropping scenario is at the member state level since some crops are only grown in distinct geographies.

The soil map of Europe contains the attribute, 'dominant use' for each STU. The respective parameter is important to consider when selecting particular soil units. However, this parameter cannot be used to visualize land use spatially since it only describes the land use which is likely to be sustained by this soil unit. Dominant use from the European soil map should not be confused with Corine Land Cover information, which is based on remote sensing data.

13.2.2 Original classification of agricultural zones by FOCUS (2000)

13.2.2.1 Climate

The FOCUS groundwater group defined nine climate regions, which represent the majority of arable land in the EU. Note that the selected scenario locations are 'virtual' scenarios. As a part of the process for defining scenarios, target values for mean annual rainfall and temperature were set by the FOCUS group. To achieve these target values some weather scenarios were scaled up to reach the desired target volume for rainfall in the defined agricultural region. For the same reason a lower rainfall volume was assigned to other scenarios. The practical implication of this pragmatic procedure was that original MARS rainfall data did not match the assigned target rainfall volume at the scenario location; in other words, some scenarios represent a climate which is not found at the scenario location but in other major agricultural areas.

Table 13-3. Classification of climate properties of major agricultural areas in the EU according to FOCUS (2000)

No. of zone	Annual Precipitation (mm)	Mean annual temperatures °C	Arable land[#] (%)	Representative location
1	600 – 800	5 – 12.5	31	Hamburg, Châteaudun
2	800 – 1000	5 – 12.5	18	Kremsmünster
3	1000 – 1400	5 – 12.5	15	Okehampton
4	600 – 800	> 12.5	13	Sevilla[§]/Thiva[§]
5	800 - 1000	> 12.5	9	Piacenza
6	< 600	> 12.5	4	Sevilla[±]/Thiva[±]
7	< 600	5 – 12.5	3	Châteaudun[±]
8	1000 – 1400	> 12.5	3	Porto
9	< 600	< 5	1	Jokioinen
10	> 1400	5 – 12.5	1	
11	1000 - 1400	< 5	1	
12	600 – 800	< 5	1	No location defined
13	800 – 1000	< 5	0	
14	> 1400	< 5	0	
15	> 1400	> 12.5	0	

[#] relative to total arable land in the EU, Switzerland and Norway

[§] rainfall amounts correspond to irrigation scenarios

[±] rainfall amount correspond to non-irrigated scenario

A first classification of Europe according to the definition of FOCUS (2000) reveals that almost the entire continent is covered by the defined climate zones shown by Table 13-3. Also new member states seem to fall well within the defined climate zones. Note that some scenarios are irrigated and thus show variable rainfall volumes as a function of crops. In this way the Châteaudun scenarios represents Region 1 as well as Region 7 when looking at annual average rainfall volumes and temperatures only. The presence of irrigation files in FOCUS scenarios thus prevents a direct comparison of climate properties. Therefore, Figure 13-3 shows only target climate zones for which leaching scenarios were developed by FOCUS (2000).
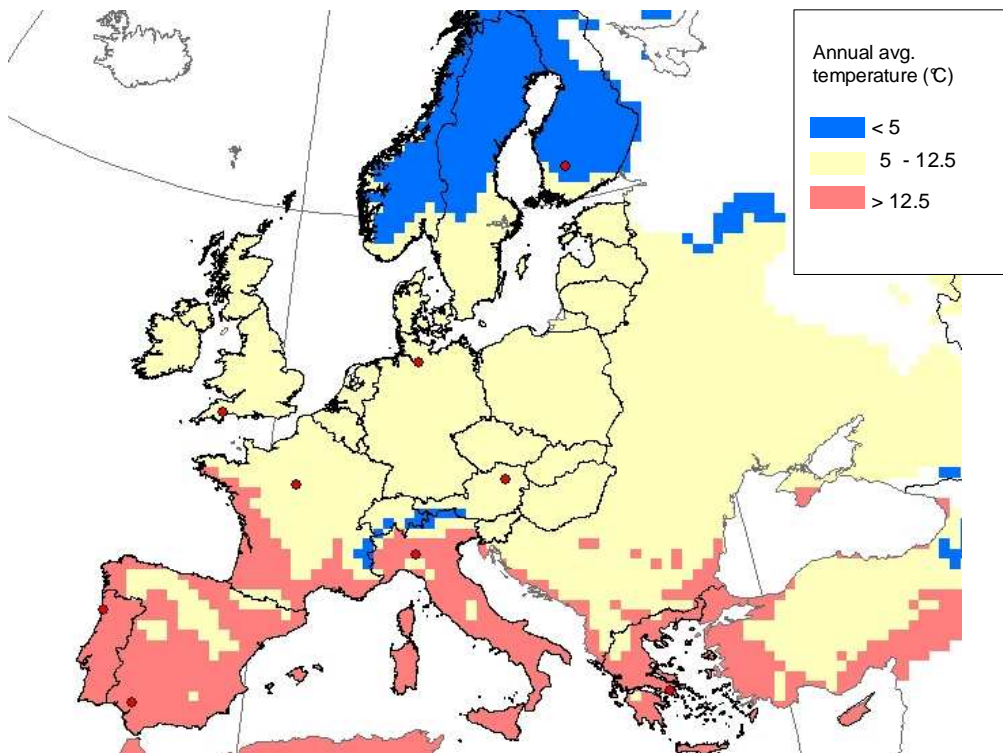
Figure 13-2. Annual average temperature in FOCUS (2000) climate zones.
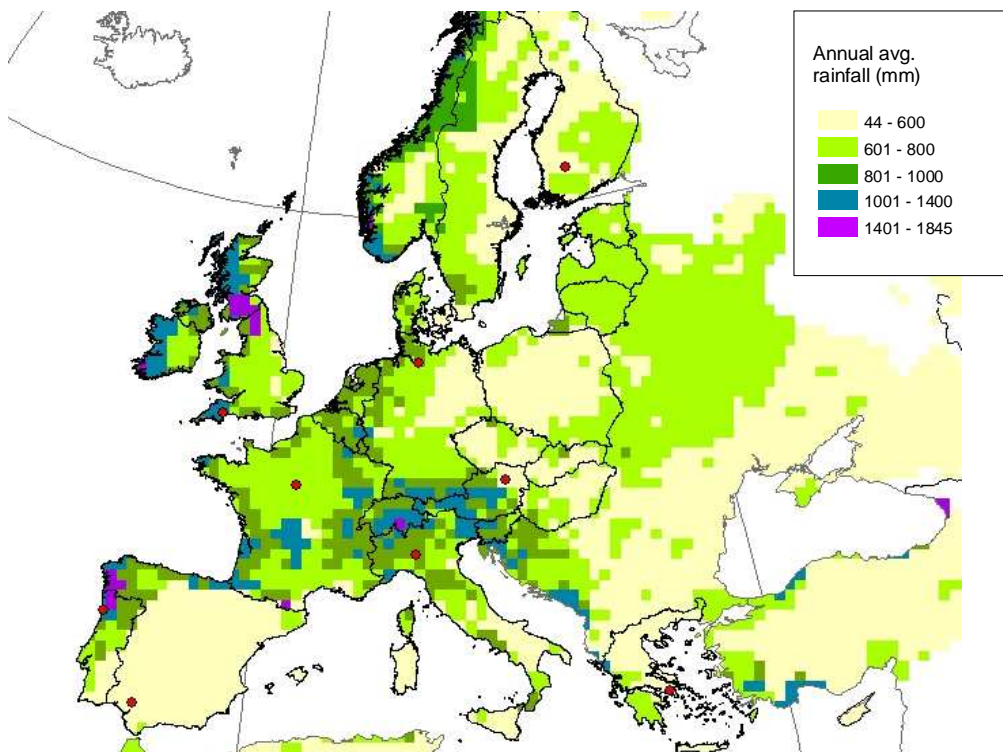
Figure 13-3. Annual average rainfall in FOCUS (2000) climate zones.

218
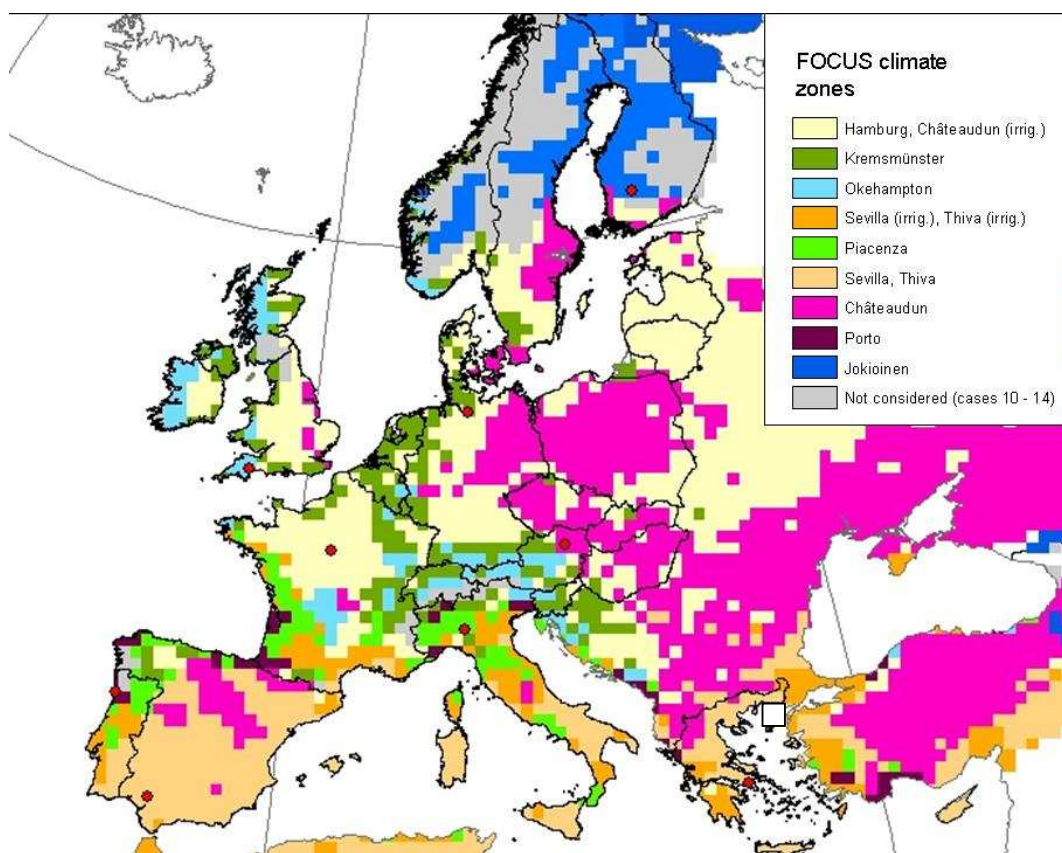
Figure 13-4. Climate zones according to the definition of FOCUS (2000). Overlay of temperature and rainfall classes. For the definition of zones refer to Table 13-3.

13.2.2.2 Soil properties

For each climate zone a representative soil profile was selected by FOCUS (2000). The intent was to define a generalized soil profile which should be significantly more vulnerable than the median soil in the region (FOCUS, 2000).

Table 13-4 gives an overview of FOCUS soil properties and the corresponding organic carbon and texture classes in the EU soil map. The EU soil map provides a dominant and secondary class texture class. In this assessment only the dominant class was considered. If the secondary texture class would have been used as well, the resulting 'coverage' for each location is slightly larger. In some cases the dominant texture class of a soil unit is different to the texture class of the location but the secondary class is the same. As a result the limitation to the dominant class results in smaller scenario areas and is thus more conservative.

Table 13-4. Classification of FOCUS soil profiles

Location	% OC in Topsoil (20 cm)	Texture (USDA)	Texture class in EU soil map
Châteaudun	1.4	Silty clay loam	Medium fine (clay < 35 % and sand < 15 %)
Hamburg	1.5	Sandy loam	Coarse (clay < 18 % and sand > 65 %)
Jokioinen	4.1	Loamy sand	Coarse (clay < 18 % and sand > 65 %)
Kremsmünster	2.1	Loam/silt loam	Medium (18 % < clay < 35 % and sand > 15 %, or clay < 18 % and 15 % < sand < 65 %)
Okehampton	2.2	Loam	Medium (18 % < clay < 35 % and sand > 15 %, or clay < 18 % and 15 % < sand < 65 %)
Piacenza	1.0	Loam	Medium (18 % < clay < 35 % and sand > 15 %, or clay < 18 % and 15 % < sand < 65 %)
Porto	3.8	Loam	Medium (18 % < clay < 35 % and sand > 15 %, or clay < 18 % and 15 % < sand < 65 %)
Sevilla	0.9	Silt loam	Medium (18 % < clay < 35 % and sand > 15 %, or clay < 18 % and 15 % < sand < 65 %)
Thiva	0.8	Loam	Medium (18 % < clay < 35 % and sand > 15 %, or clay < 18 % and 15 % < sand < 65 %)
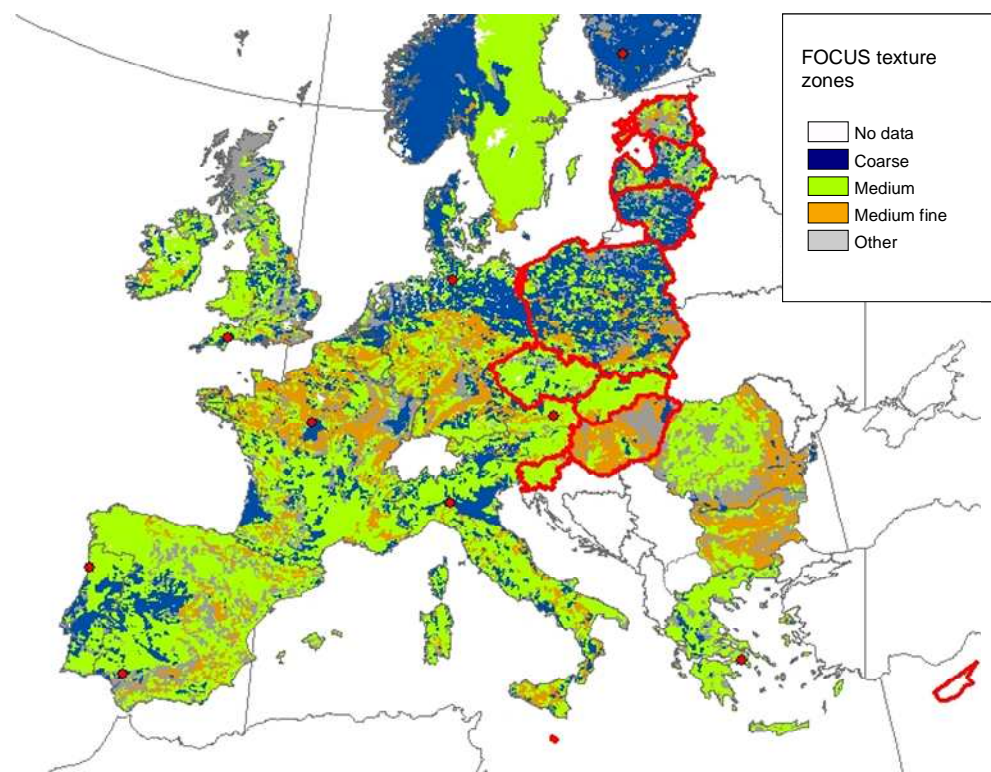
Figure 13-5. Soil texture classes according to FOCUS (2000). For the definition of the classes refer to Table 13-4.
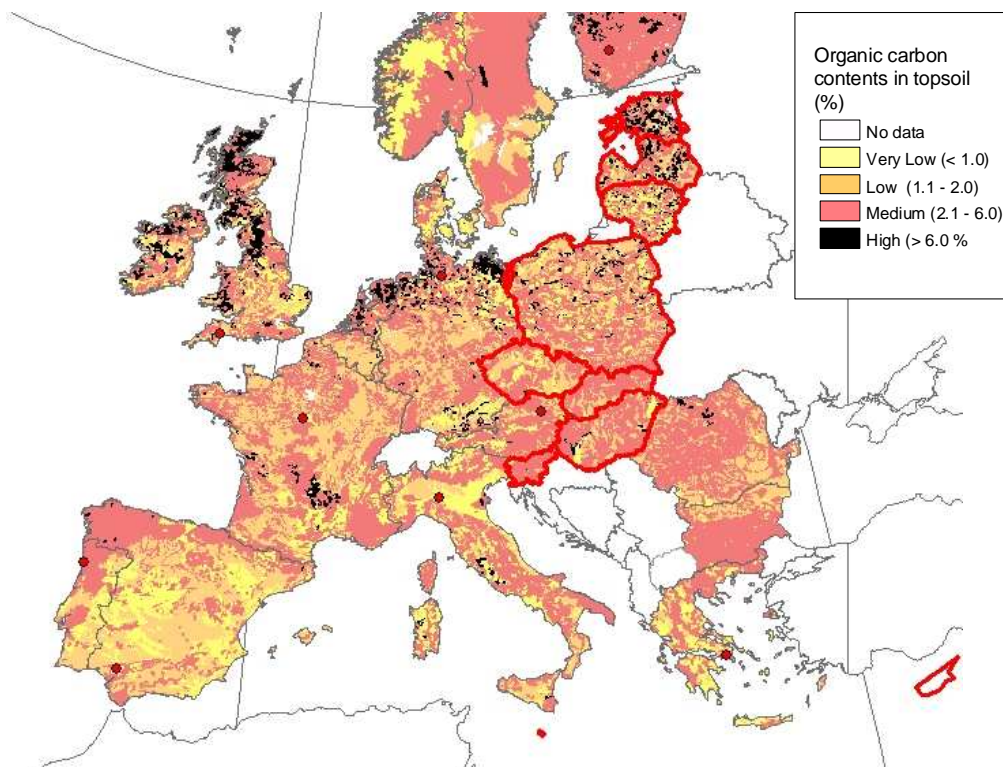
Figure 13-6. Soil organic carbon classes as provided by the EU soil map.

Current FOCUS soil profiles represent coarse and medium textured soils and thus reflect the majority of European soils. In some regions finer textured soils - with clay contents > 35 % - occur. Hungary shows the highest fraction of fine textured soils in relation to total area amongst all NMCs. (Cyprus is not covered by the present version of the EU soil map.)

13.2.2.3 Crops

Each FOCUS scenario was parameterized for a specific group of crops. The EU soil map provides information whether a certain STU is sustaining these crops. Most agricultural soils were classified as 'arable land'. In some cases a more specific classification is provided (e.g. horticultural soil, vineyards etc.).

In a detailed spatial assessment of leaching vulnerability, the soils should be restricted to only those which can be potentially used for plant production. A list of representative classes of soil use for the various FOCUS crop scenarios is given in Table 13-5.

Table 13-5. Crops represented by FOCUS leaching scenarios (from Hollis, 2004).

Location	Specified crops	STU land use classes
Châteaudun	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; winter oil seed rape; spring cereals; maize; cabbage; carrots; onions; peas (animals); tomatoes; apples; vines.	3; 6; 7; 12; 13; 16
Hamburg	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; winter oil seed rape; spring cereals; maize; cabbage; carrots; onions; beans (field); peas (animals); strawberries; apples; vines.	3; 6; 7; 12; 13; 16
Jokioinen	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; spring oil seed rape; spring cereals; cabbage; carrots; onions; peas (animals); bush berries; strawberries; apples.	3; 6; 12; 13; 16
Kremsmünster	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; winter oil seed rape; spring cereals; maize; cabbage; carrots; onions; beans (field); strawberries; apples; vines	3; 6; 7; 12; 13; 16
Okehampton	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; winter oil seed rape; spring cereals; spring oil seed rape; linseed; maize; beans (field); peas (animals); apples;	3; 6; 12; 13; 16
Piacenza	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; winter oil seed rape; maize; soyabean; sunflower; tobacco; tomatoes; apples; citrus; vines	3; 6; 7; 12; 13; 16; 21
Porto	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; winter oil seed rape; spring cereals; spring oil seed rape; maize; beans (veg); cabbage; carrots; onions; tomatoes; apples; citrus; vines	3; 6; 7; 12; 13; 16; 21
Sevilla	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; maize; cabbage; tomatoes; sunflower; strawberries; citrus; apples; vines; cotton.	3; 6; 7; 12; 13; 15; 16; 21
Thiva	Grass (+ alfalfa); potatoes; sugar beet; winter cereals; maize; beans (veg); cabbage; carrots; onions; tomatoes; citrus; apples; vines; tobacco; cotton.	3; 6; 7; 12; 13; 15; 16; 21

13.2.3 Criteria used for the assessment of scenarios

In a strict sense each crop would require a separate assessment of worst-case weather properties under which it can potentially be grown. The methods presented in this paper nevertheless neglect the spatial distribution of individual crops in an attempt to provide a generic assessment of climate and soil properties in NMCs with respect to current FOCUS leaching scenarios.

The assessment was carried out on the basis of 20-year weather series that were compiled for existing FOCUS leaching scenarios. From these weather series a 'worst-case' and a 'best case' weather year can be extracted by means of the following criteria:

- The year in which the highest rainfall volume coincides with the lowest temperature is defined as the worst-case weather year. The respective combination of rainfall and temperature sets the upper boundary of climate vulnerability that is represented by the scenario.
- The year in which the lowest rainfall volume coincides with the highest temperature is defined as the best-case weather year. The respective combination of rainfall and temperature sets the lower boundary of climate vulnerability that is represented by the scenario.

Note that only existing combinations of temperature and rainfall were assessed. This method avoids the use the global maximum rainfall and global minimum temperature when this combination did not occur during the same year.

Upper and lower boundaries of climate vulnerability were subsequently used to visualize cropping areas which fall into the same climate zone. The spatial query identifies all cells where the combination of average temperatures and rainfall sums is between the upper and lower boundaries for the given scenario. The respective boundary values are given in Table 13-6.

As a refinement of the original definition of FOCUS only rainfall volumes between October and March where considered. This approach is based on the following rationale:

- Ground water recharge is most likely occurring outside the vegetation period when evapotranspiration is low and soil moisture is close to saturation. Northern European soils are typically saturated after autumn rainfalls and again at the end of winter

during snowmelt. A similar cycle can be observed in southern Europe although the absolute volume of ground water recharge is smaller.

- From spring until late summer the overall water balance is likely to be negative for most agricultural areas in Europe. A rough calculation of water excess (precipitation minus evapotranspiration) during April and September reveals that only in small regions the water balance is positive in summer (Figure 13-7).

A further advantage of this pragmatic approach is that uncertainties with regards to irrigation practices during the vegetation period are minimized.

Table 13-6. Range of temperature and rainfall volume in current FOCUS scenarios

Location	Boundary	Annual avg. temperature (°C)	Rainfall Oct – March (mm)	Occurring in year	*Annual rainfall (mm)#*
Châteaudun	Upper	10.7	492	11	*787*
	Lower	12.4	232	2	*413*
Hamburg	Upper	8.3	530	13	*941*
	Lower	10.3	286	2	*608*
Jokioinen	Upper	2.1	317	17	*745*
	Lower	5.8	212	2	*394*
Kremsmünster	Upper	8.0	485	13	*1096*
	Lower	8.9	134	2	*312*
Okehampton	Upper	9.3	627	11	*1097*
	Lower	11.0	450	4	*1132*
Piacenza	Upper	12.2	645	10	*1101*
	Lower	14.2	337	15	*574*
Porto	Upper	14.4	1191	9	*1563*
	Lower	15.1	482	5	*864*
Sevilla	Upper	16.9	562	8	*809*
	Lower	19.6	202	6	*277*
Thiva	Upper	15.7	558	8	*651*
	Lower	17.2	257	6	*315*

Not used in this assessment
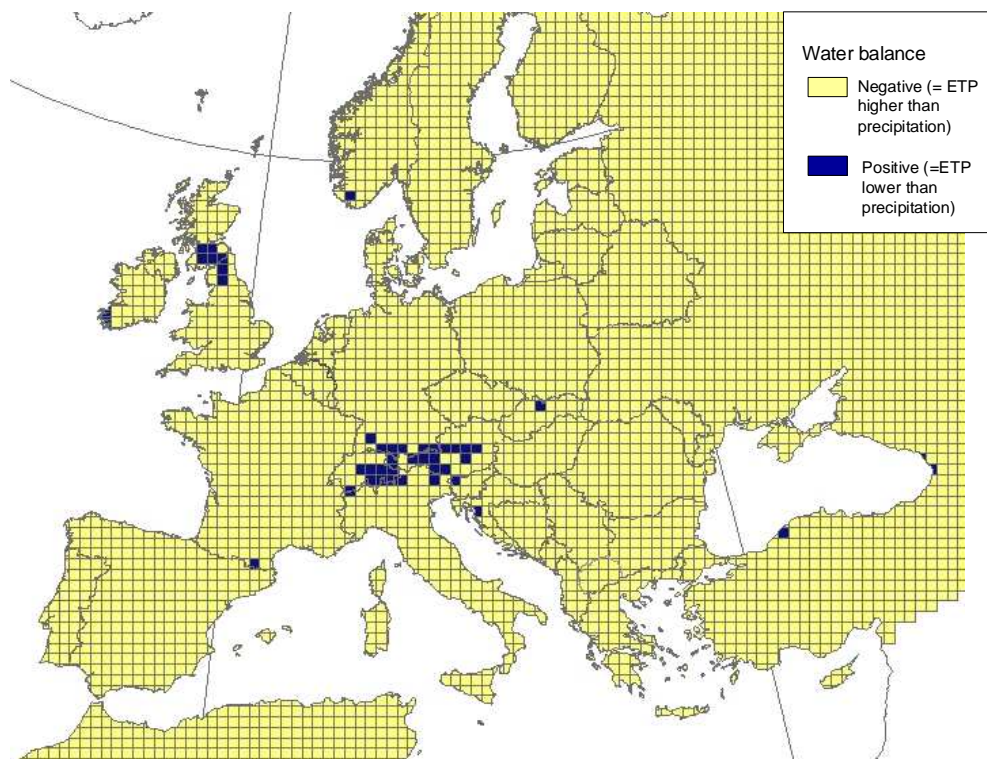
Figure 13-7. Calculated water balance based on evapotranspiration and precipitation from April – September (11-year, 8-year average)

13.3 Results and discussion

The geographic extension of each FOCUS leaching scenario was identified by means of spatial queries as shown in Table 13-7. Since several zones overlap, showing all zones in one single map is not appropriate. Figures 13-8 through 13-16 show the spatial extension of FOCUS leaching scenarios. All non-agricultural areas were eventually masked out by means of an overlay with Corine Land Cover (see Table 13-7 for relevant land use classes in Corine).

Note that both the European Soil Map as well as Corine Land Cover use the attribute "land use". The European Soil Map gives the potential land use for each soil unit whereas Corine gives the real land cover, which was determined on the basis of remote sensing data. The overlay of both database gives finally a soil unit which potentially sustains arable use (= information in EU soil map) and is also covered by arable crops at the time of this study (= information from Corine Land Cover, status of 2004).

Table 13-7. Spatial queries to identify the geographic extension of FOCUS scenarios by overlaying three GIS data bases.

| Location | MARS Climate Data | | | | EU Soil Map | | | | | Corine Land Cover Class* |
| | Average Winter Rainfall (mm) | | Annual Average Temperature (°C) | | Organic Carbon | | Texture | | Land Use# | |
	min	max	min	max	(%)	class	class	code		
Hamburg	286	530	8.3	10.3	1.5	Low	Sandy loam	1	3; 6; 7; 12; 13; 16	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2
Châteaudun	232	492	10.7	12.4	1.4	Low	Silty clay loam	3	3; 6; 7; 12; 13; 16	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2
Jokioinen	212	317	2.1	5.8	4.1	Medium	Loamy sand	1	3; 6; 12; 13; 16	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.2
Kremsmünster	134	485	8.0	8.9	2.1	Medium	Loam/ silt loam	2	3; 6; 7; 12; 13; 16	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2
Okehampton	450	627	9.3	11.0	2.2	Medium	Loam	2	3; 6; 12; 13; 16	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.2
Piacenza	337	645	12.2	14.2	1.0	Very low	Loam	2	3; 6; 7; 12; 13; 16; 21	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2
Porto	482	1191	14.4	15.1	3.8	Medium	Loam	2	3; 6; 7; 12; 13; 16; 21	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2
Sevilla	202	562	16.9	19.6	0.9	Very low	Silt Loam	2	3; 6; 7; 12; 13; 15; 16; 21	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2; 2.2.3
Thiva	257	558	15.7	17.2	0.8	Very low	Loam	2	3; 6; 7; 12; 13; 15; 16; 21	2.1.1; 2.4.1; 2.4.2; 2.4.3; 2.2.1; 2.2.2; 2.2.3

See Table 13-5 for a detailed description of land use classes in the European Soil Database.

* See Appendix 8 (Table A8-2) for a detailed description of land use classes in the Corine Land Cover Database.

Note that the EU soil data base uses different codes for land use classes than Corine Land Cover.

The spatial queries are illustrated in the example for Châteaudun. This location 'covers' all areas in new member countries that comply with the following criteria:

- Average rainfall amounts and temperatures are between the worst and best weather year in Châteaudun. The best-case year had 232 mm winter rainfall and a temperature of 12.4 °C, the worst-case year had 492 mm winter rainfall and 10.7 °C temperature. All areas where such conditions occurred between 1992 and 2002 (the time series available in MARS) are classified as 'climate zone Châteaudun'.

- The content of organic carbon is 1.4 % or higher and soil texture class is 3 or higher (finer textured). All areas that comply with these criteria are classified as 'soil region Châteaudun'. Note that only soils with agricultural land use were considered.

- Any area where the climate zone and soil region Châteaudun co-occur is classified as 'scenario area Châteaudun'

13.3.1 Coverage of Accession countries by existing FOCUS scenarios

13.3.1.1 Estonia

The Jokioinen location represents well Estonian climate conditions. Prevailing low temperatures sustain high organic carbon contents in topsoils, which are reflected in a similar way by the Jokioinen scenarios.

13.3.1.2 Latvia

A similar conclusion as for Estonia applies to Latvia. Soils with very high contents in organic matter are frequent although cover a slightly smaller fraction of arable land than in Estonia. For that reason more soil units appear to be similar rather than less vulnerable than Jokioinen.

13.3.1.3 Lithuania

The climate of northern Lithuania is still similar to Jokioinen and most soils have either similar or less vulnerable soil properties. The larger part of the country is however warmer and therefore better represented by Hamburg and Kremsmünster climate. The more humid Hamburg climate is most representative for regions close to the Baltic Sea. Some areas which are influenced by more continental climate conditions are dryer than 'Hamburg' but show coarser textured soils or lower organic carbon contents than e.g. the 'Kremsmünster' scenarios. For that reason the 'Hamburg' scenarios should be assessed to determine whether they are sufficiently conservative to cover also those areas which have a different rainfall regime but a similar coarse texture.

13.3.1.4 Poland

Coarse textured soils are primarily found in the northern part of the country. This area shows also very similar climate properties to Hamburg suggesting that this location represents northern Poland to a sufficient extent. Large parts of Poland fall within the Kremsmünster climate zone. Some areas are neither represented by Hamburg nor Kremsmünster, in most cases because the prevailing soil types are coarser than 'Kremsmünster' soil or have a lower organic carbon content.

13.3.1.5 Czech Republic

The majority of soils belong to a similar texture class like Kremsmünster. Also organic carbon contents are in most cases similar to these scenarios. A few coarse textured soils with less OC are well represented by the Hamburg scenarios. A small region in central Bohemia and around Prague seems to have different soil characteristics than those of Kremsmünster although its climate properties are closer to Kremsmünster than Hamburg.

13.3.1.6 Slovakia

The largest part of Slovakia is represented by Kremsmünster climate whereas Hamburg is only representative for smaller areas. Similar conclusions as to Czech Republic apply to Slovakia in terms of representativeness of Kremsmünster soil properties for some parts of Slovak agriculture.

The southernmost part around Bratislava and along the Danube River belongs to a climate zone represented by the Châteaudun. Also soil properties seem to be similar or less vulnerable than this location.

13.3.1.7 Hungary

The EU soil map shows a high density of fine textured soils in Hungary. Organic carbon contents are typically higher than 1.5 – 2 %. For that reason large parts of the country are well represented by the soil in the Châteaudun scenarios. Also climate properties are very similar to Châteaudun. None of the other locations seem to better represent Hungarian soil and climate conditions.

13.3.1.8 Slovenia

Slovenia is located in a transitional climate which is closer to northern than southern European weather conditions, although overall temperatures are at the upper boundary of those found in northern Europe. Rainfall amounts in winter are close to amounts reflected by the Okehampton, Hamburg, Kremsmünster, Châteaudun, and Piacenza scenarios. Annual

average temperatures for Piacenza are however consistently higher than in Slovenia; therefore Piacenza does not seem to be representative for Slovenian climate conditions.

The vast majority of Slovenian soils are medium textured with moderate to medium organic carbon contents. Therefore, the Châteaudun, Okehampton, and Kremsmünster locations appear to be most suitable to represent soil and climate conditions in Slovenia. Hamburg represents a suitable climate range but is conservative in terms of soil properties.
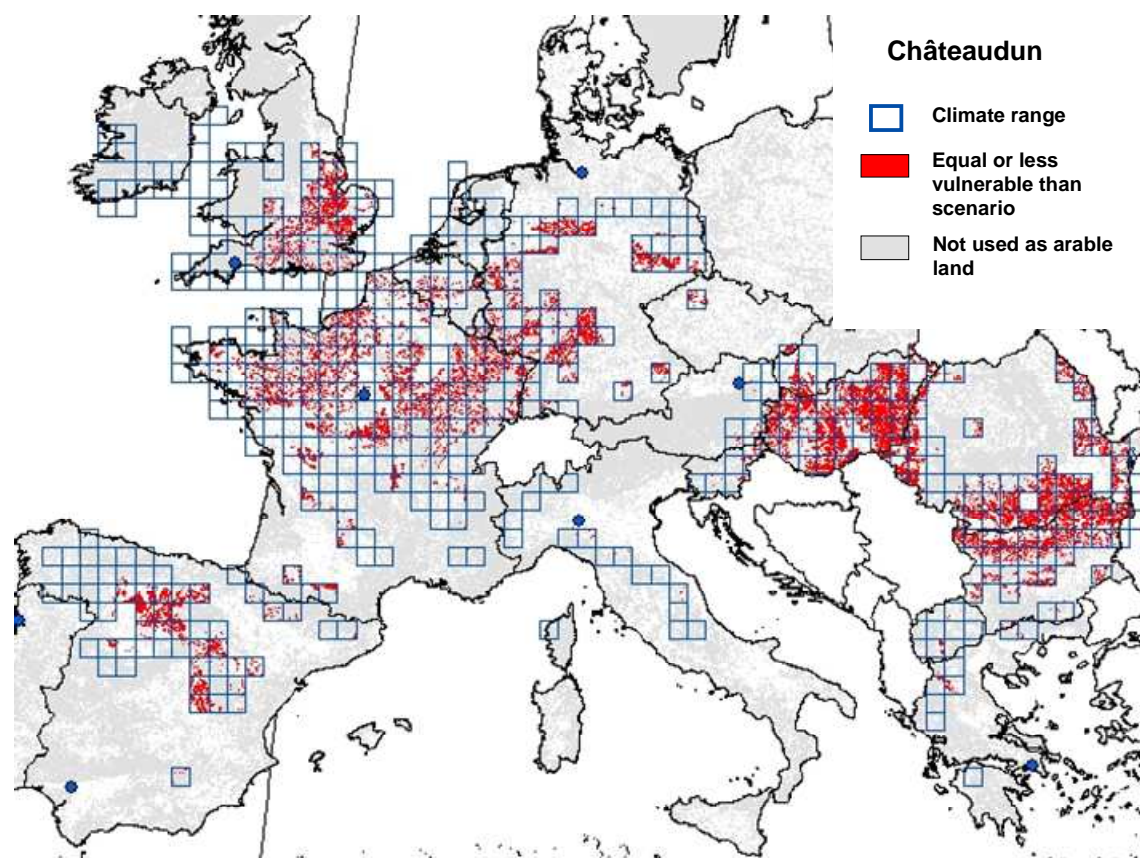
Figure 13-8. Extension of the 'Châteaudun' scenarios. In this figure arable land includes orchards and vineyards (see Table 13-7).
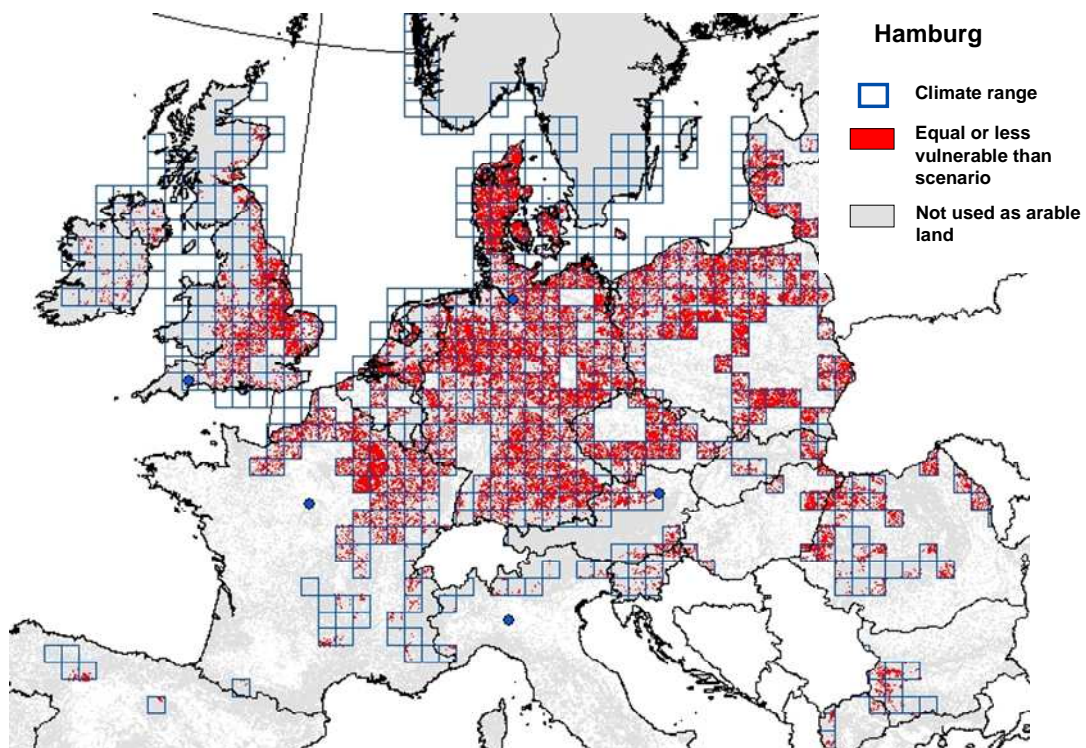
Figure 13-9. Extension of the 'Hamburg' scenarios. In this figure arable land includes orchards and vineyards (see Table 13-7).
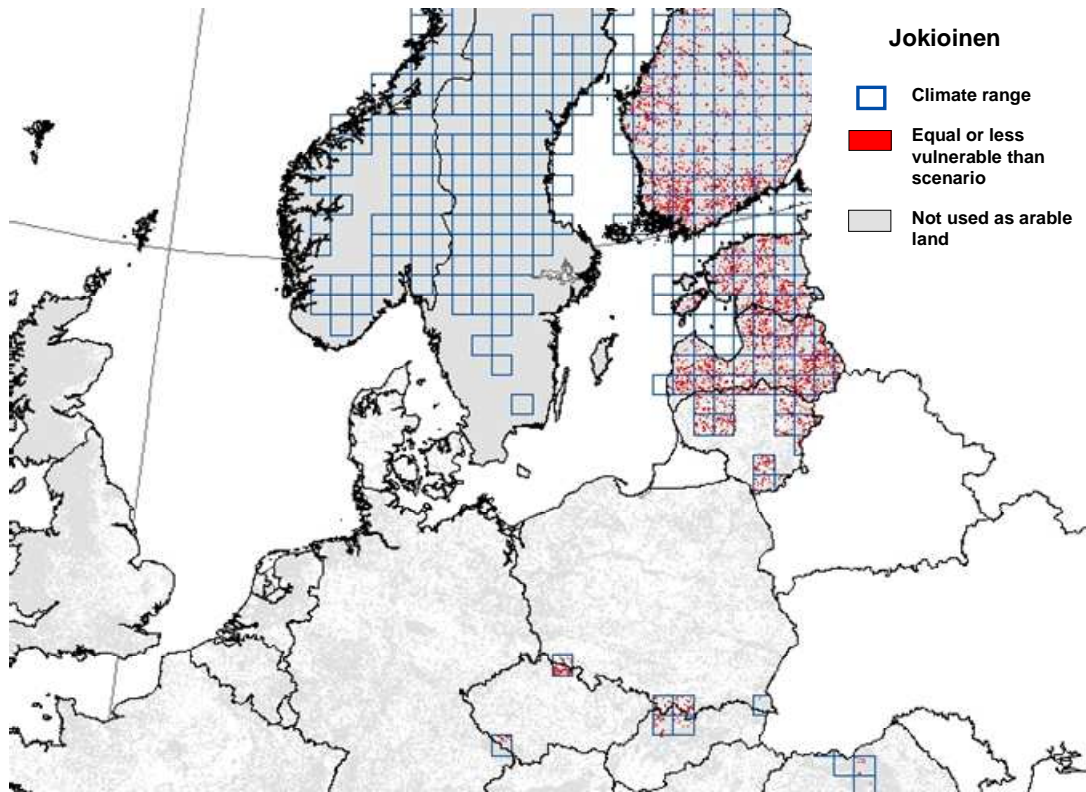
Figure 13-10. Extension of the 'Jokioinen' scenarios. In this figure arable land includes orchards (see Table 13-7).
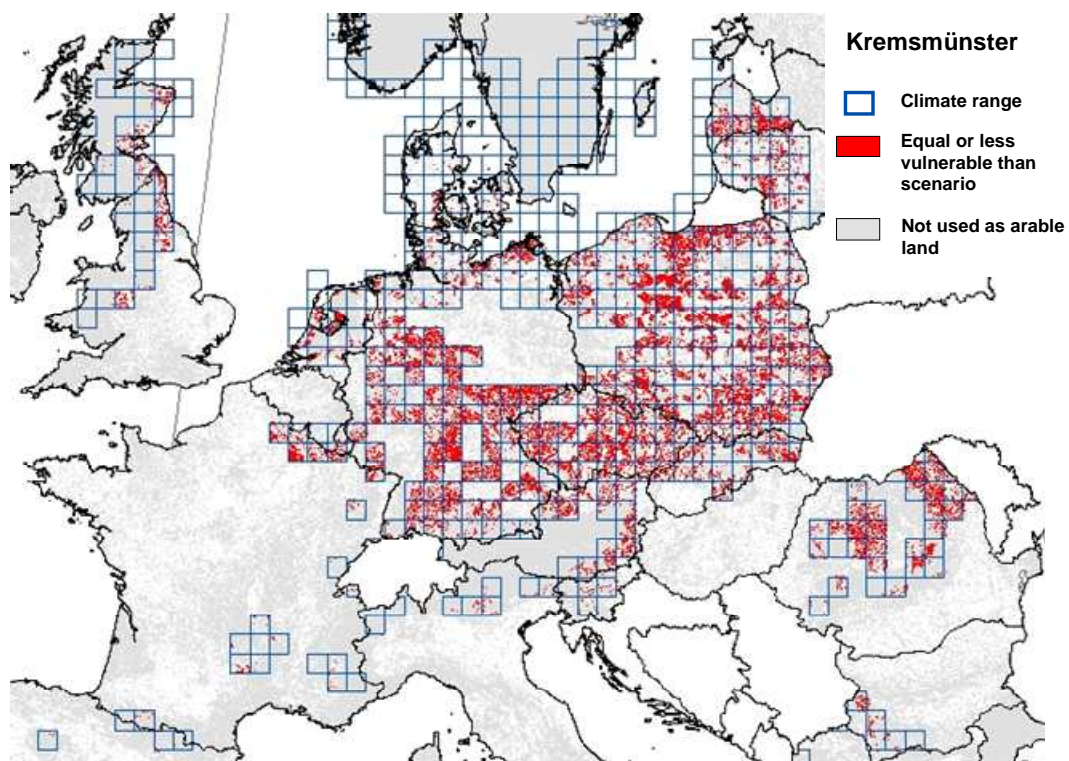
Figure 12-11. Extension of the 'Kremsmünster' scenarios. In this figure arable land includes orchards and vineyards (see Table 13-7).
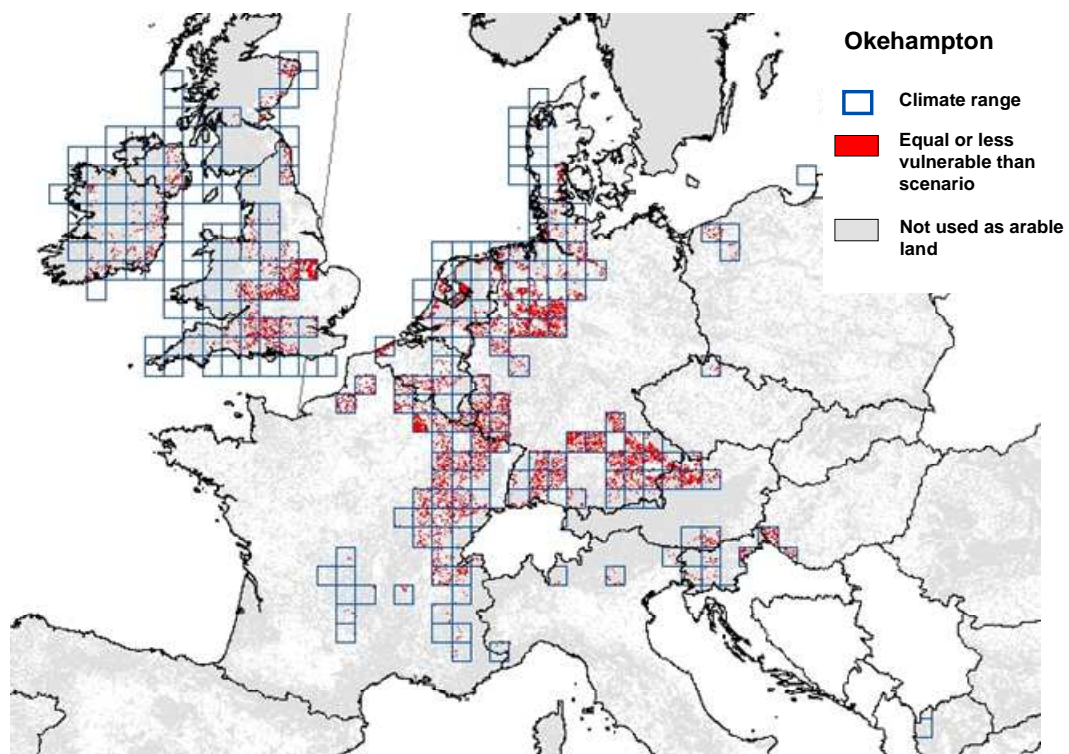
Figure 13-12. Extension of the 'Okehampton' scenarios. In this figure arable land includes orchards (see Table 13-7).
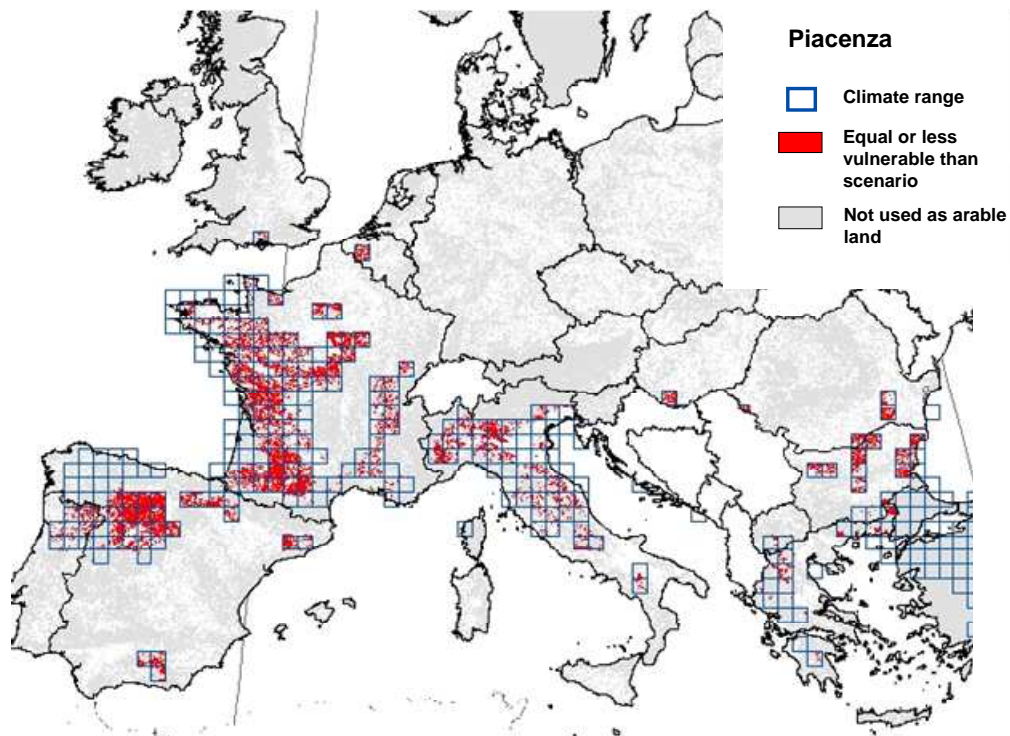
Figure 13-13. Extension of the 'Piacenza' scenarios. In this figure arable land includes orchards and vineyards (see Table 13-7).
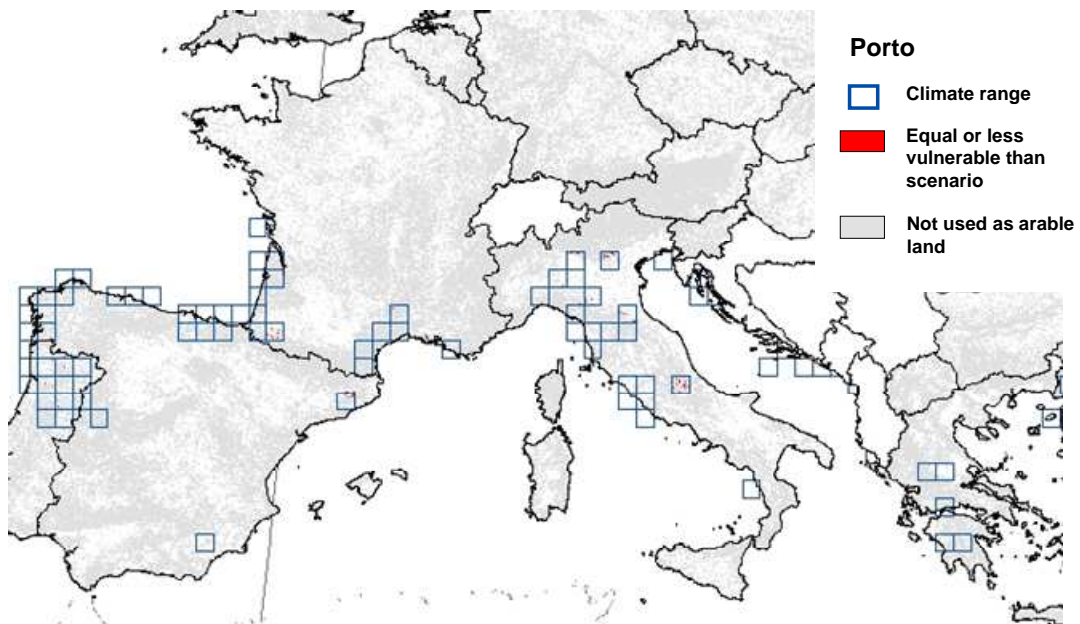
Figure 13-14. Extension of the 'Porto' scenarios. In this figure arable land includes orchards and vineyards (see Table 13-7).
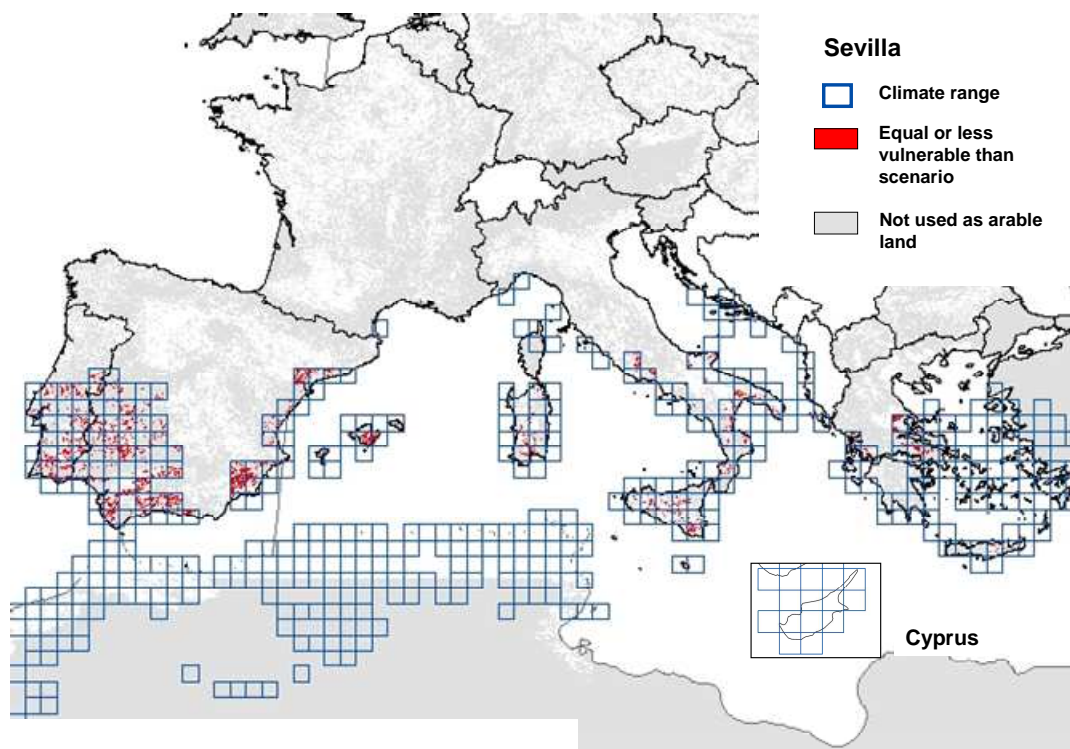
Figure 13-15. Extension of the 'Sevilla' scenarios. In this figure arable land includes orchards, olives, and vineyards (see Table 13-7).
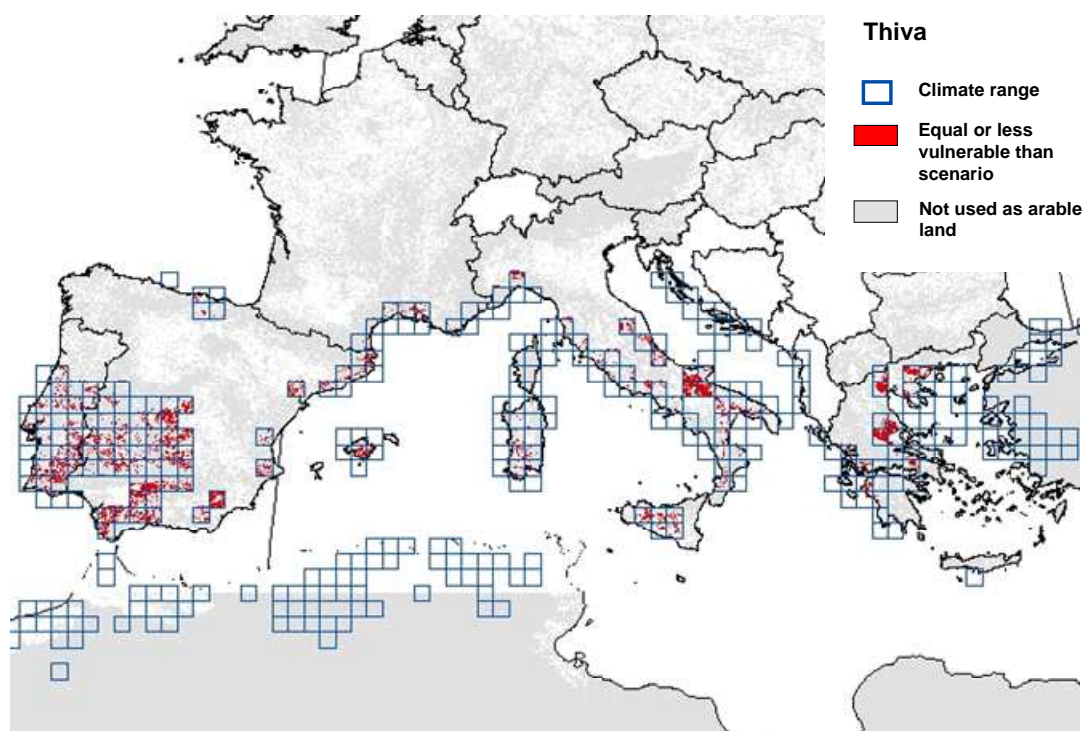
Figure 13-16. Extension of the 'Thiva' scenarios. In this figure arable land includes orchards, olives, and vineyards (see Table 13-7).

233

13.3.1.9 Malta

Sevilla is most representative for soil and climate conditions in Malta. In most years annual average temperatures are even higher than in 'Sevilla' because of more temperate winters.

13.3.1.10 Cyprus

Cyprus is not covered by the present version of the EU soil map therefore only a preliminary conclusion can be drawn with regard to the applicability of climate scenarios. Based on the spatial queries conducted with climate data only the 'Sevilla' appears to be representative for Cyprus.

13.3.2 Conclusions on the applicability of FOCUS scenarios to new member states

The analysis revealed that three FOCUS locations contain combinations of soil and climate properties that are not found in new member states. The respective locations are Thiva, Piacenza and Porto. Porto is representative of the least area, as presented in detail in Section 11.2.2. All other locations cover major agricultural areas in new member states should therefore be applicable to new member countries for screening simulations at Tier 1.

Table 13-8. Summary of locations which are representative of soil and climate conditions in new member countries.

Country	Châteaudun	Hamburg	Jokioinen	Kremsmünster	Okehampton	Sevilla
Estonia			X			
Latvia			X			
Lithuania		X	X	X		
Poland		X		X		
Czech Republic		X		X		
Slovakia	X	X		X		
Hungary	X					
Slovenia	X	X		X	X	
Malta						X
Cyprus						X

13.3.3 Areas for which further analysis is needed

Some smaller areas in NMCs exhibit soil and climate conditions that deviate from the criteria set for the purpose of this assessment. A first evaluation of these regions indicated that organic carbon contents in topsoils are an important reason for these deviations. A major uncertainty is the occurrence of soils with lower organic carbon contents than 'Kremsmünster' within the 'Kremsmünster' climate range.
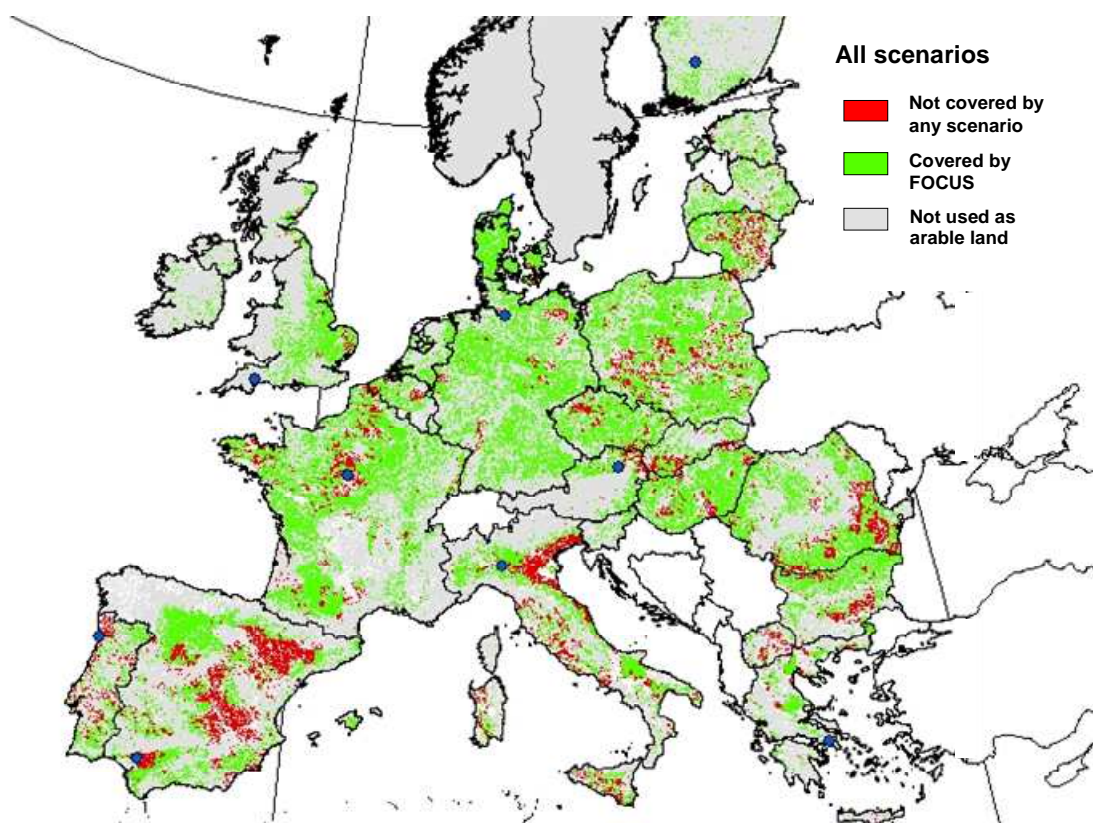
Figure 13-17. Areas requiring further analysis. In this figure arable land includes orchards, olives, and vineyards.

An attempt was made to analyse the nature of missing areas, using Lithuania as an example. Lithuania falls mostly within the Hamburg, Kremsmünster and Jokioinen climate zones. Among these locations Hamburg and Jokioinen show a coarse soil texture whereas Kremsmünster is defined to be a loam to silt loam soil. As a consequence those parts of the country which are only covered by the Kremsmünster climate zone are not covered by the Kremsmünster soil scenario because the soil texture is more vulnerable for leaching. Figure 13-16 shows the result of this simple overlay.

Then the organic carbon contents were examined to determine if they were lower than the organic carbon content of the Hamburg soil. The results of this analysis are shown in Figure 13-19.

Legend:
- Hamburg or Jokioinen climate
- Kremsmünster climate
- Texture class 1 covered by Hamburg and Jokioinen climate
- Other soils covered by Hamburg and Jokioinen climate
- Non-agricultural land
- No data
- Texture class 1 not covered
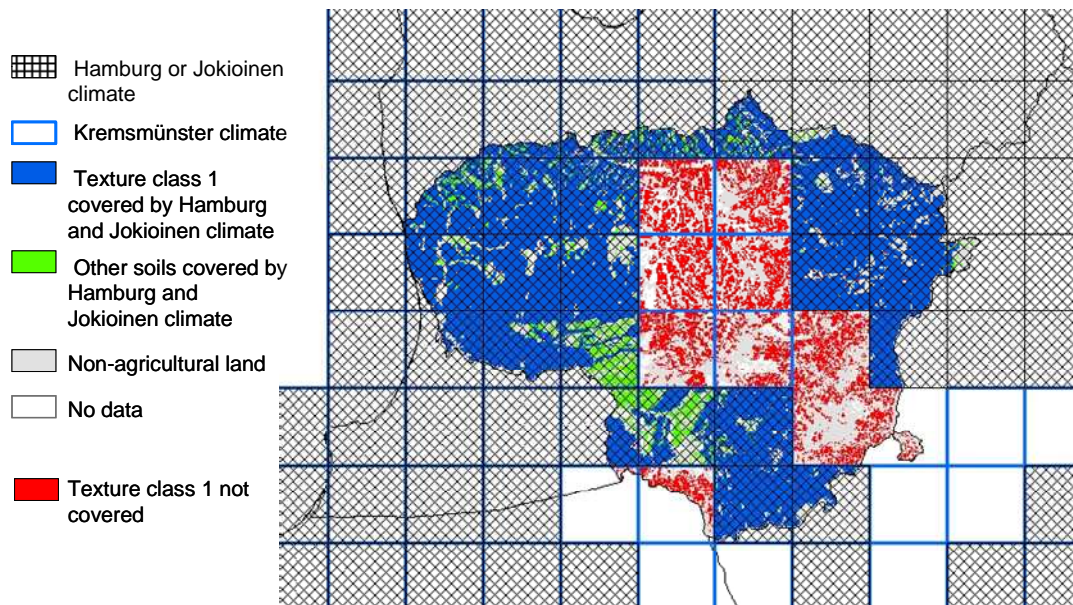
Figure 13-18. Area in Lithuania that is not covered by the current set of FOCUS scenarios.

Figure 13-19 shows that most soils in the area of interest have an organic carbon content of > 1.5% and the Hamburg soil profile would be protective for this area, with the exception of some scattered soil units that have lower organic carbon contents.

A small region in the Eastern part of Lithuania is not covered by any scenario because annual average temperature (6.7 – 6.9 °C) is lower than the temperature at Hamburg and Kremsmünster but higher than the temperature at Jokioinen.

Not covered by any climate scenario

Legend:
- Kremsmünster climate
- Texture class 1 and OC is lower than Hamburg scenario
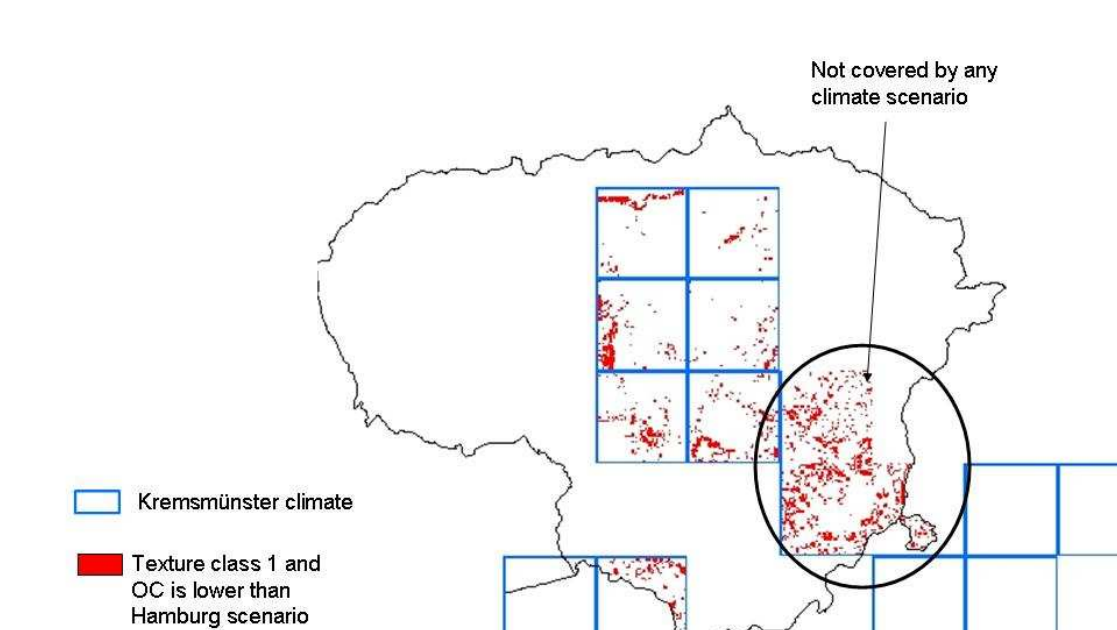
Figure 13-19. Soil units in Lithuania not covered by the current set of FOCUS scenarios.

236

13.4 Conclusions

The spatial analysis shows that the current set of FOCUS leaching scenarios is applicable to new member countries for the purpose of Tier 1 screening simulations. Some smaller areas are not covered by current scenario properties and an example is presented of how the missing area might be characterised.

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APPENDIX 1. QUESTIONNAIRE SENT TO MEMBER STATES

Questionnaire to be answered by Member States

Regarding routines in national ground water risk assessment of plant protection products on a Member State Level

<u>Aim of the questionnaire</u>

The FOCUS groundwater group has been set up by the Commission in order to improve the current leaching assessment of PPPs at the EU level. As a first step in this activity, a questionnaire is being sent out to all member states to get feedback on the opinion of the current EU scheme and to have an inventory of methods used to assess the risk to groundwater at a member state level.   It is hoped that by collecting this information the current method of assessment can be expanded and improved, potentially leading to greater harmonization of leaching assessment in Europe.
Most of the questions will be possible to answer by choosing among proposed alternatives, while some questions need an explanatory answer. The questionnaire will be divided in general questions and detailed questions. Prior to each section the current EU approach is summarised for ease of reference.

Please indicate questions where there is a choice by overwriting the choice by <mark>yellow</mark>.
In the other cases answer as briefly as possible.

<u>If you have any questions</u> regarding this questionnaire, please, send them to on of the following FOCUS members:
Bernhard Gottesbüren
Karin Hanze
Ralf Fischer

To be able to get back to the individual Member State for further clarifications, please give name and e-mail address to a contact person who is concerned with ground water risk assessment:

This answer comes from:

Member State …………………………………………………..

Contact person, Name: …………………………………..
E-mail: ………………………………..

When you have answered the questionnaire, please, send it back to:

Thank you for cooperation.

Date of answer: …………………………………………………

1. General questions

EU Approach

In the framework of the evaluation of active substances with regard to their inclusion in Annex I to Directive 91/414/EEC, the assessment of risk to groundwater is carried out according to GAP (intended use proposed and supported by the notifier) and to FOCUS GW guideline.

No trigger is used before assessment, but expert judgement.

At EU level a tiered approach is recommended but not yet specified.

Q No.	Question	National Approach
1	Does your country assess risk to groundwater as a routine before approval of a PPP in your country?	Yes Planned but not yet implemented No
2	Is the EU GW assessment as defined in the FOCUS GW guideline sufficient for the risk assessment in the authorisation procedure of PPP in your country? If your answer is No, go to Q No. 2.1	Yes No
2.1	State shortly the main reason/s why the FOCUS GW guideline is not sufficient See also questions 13, 16 and 17.	

Q No.	Question	National Approach
2.1.1 new member states only	Which GW assessment schemes do you use for national risk assessment	
2.1.2. new member states only	Do you have any training for the risk assessment to groundwater in any MS? Which of MS do you have training with?	Yes No
2.2	In order to improve the existing Tier I FOCUS groundwater scheme, have you had any technical scientific difficulties (i.e. excluding software problems) with using the existing FOCUS groundwater scenarios? Examples might be, incorrect planting dates for scenarios, or non-inclusion of specific crops in scenarios etc. If yes, please provide a detailed documentation of the difficulties. Problems that have been solved already via new versions of the software packages, do not need to be reported	
2.3 new member states only	Do you have any needs for training in Focus modelling?	Yes No

Q No.	Question	National Approach
3	What is the trigger for national assessment of risk for groundwater contamination? If other trigger than Review Report, such as a national judgement, please, answer Q No. 3.1	According to the Review Report (RR) for the active substance Other trigger:
3.1	If the trigger is according to national criteria You can give more than one answer here	Assessment in EU re-registration process did not result in recommendations in the RR, but "national" criteria" raise concerns that have to be addressed on MS level Give the criteria Give justification Earlier national assessment prior to the EU re-registration Positive findings from groundwater monitoring data Other
4	Do you assess along a tiered approach? If you answer Yes, go to Q No. 4.1	Yes No
4.1	Briefly describe the tiered approach you apply	Specify here

2 Regulatory questions

EU Approach
Endpoint according to Annex VI: 0.1 µg a.s./l in groundwater
Tier 1: 0.1 µg a.s./l, defined as the 80[th] percentile concentration derived by FOCUS modelling in the leaching water at 1 meter depth averaged over the simulation period (1 year for an annual application, 2 and 3 years for the application every 2[nd] and 3[rd] year)
Higher tiers: still to be defined

Q No.	Question	National Approach
5	How do you define the endpoint value for approval? a) Tier 1 b) At higher tiers	a) Tier 1 at depth b) Higher tiers at depth/s
6	Do you apply a safety factor on the endpoint a) For parent b) For metabolites	a) Yes, which? No b) Yes, which? No
7	Do you take decisions using model simulations only?	Yes No If No, please, specify under (20-21.2, 23-26), how other data e.g. lysimeter, field leaching studies, monitoring data are used.

8	Are the following possible alternatives to non-full-approval? a) Conditional approval? b) Regional or local approval? c) Special approval for farmers? d) Special indications?	a) Yes No b) Yes No c) Yes No d)
9	Are risk mitigation measures considered at approval on your national level?	No Yes If Yes, please describe

3 Specific questions on Scenarios

EU Approach
Reference to the guideline - FOCUS groundwater Scenarios in the EU review of active substances within the directive 91/414/EEC (SANCO/321/2000 rev. 2)

Q No.	Question	National Approach
10	Do you use any of the nine FOCUS groundwater scenarios as your national scenario? If your answer is No, go to Q No. 10.1	Yes Which? No
10.1	If you have scenario/s different from the FOCUS GW scenarios, please, state shortly the reason to that? Please, briefly state the reason.	

11	Do you have more than one national scenario?	Yes How many? No

12	Which criteria are used for the choice of national scenarios?
	a) 12.1 a. weather (rainfall)
	b) 12.1 b. weather (temperature)
	c) 12.2 soil type
	d) 12.3 crops
	
	In defining a scenarios is any of a) to d) more important than the other?
		a) - Average rainfall
		   - Worst case rainfall
		    - Weather typical for major agricultural area/s
		
		b) - Average temperature
		   - Worst case temperature
		    - Weather typical for major agricultural area/s
		
		c) - Average soil
		   - Worst case soil
		    - Soil/s typical for major agricultural area/s
		
		- Crops in general
		Crops typical for major agricultural area/s
		
		Importance

13	Do you consider your scenario/s more or less conservative than the 9 FOCUS scenarios?	More Less
14	Do you consider your national scenarios as higher tier compared to FOCUS Tier 1?	Yes Please, give a short reason No

Q No.	Question	
14.1	If you use more than one scenario, how many "passes" are required to grant authorisation or, alternatively, move to further assessment?	

4 Model

EU Approach

FOCUS GW guideline recommends 4 models, MACRO (1 macropore scenario), and PEARL, PELMO and PRZM for all 9 EU scenarios

Q No.	Question	National Approach
15	Do you have a requirement to special model/s?	Yes ? Which ? Why ?
15.1	Do you have a preference to special model?	

5 Parameterisation

EU Approach

At tier 1, the FOCUS GW guideline recommends either to use laboratory data or field data. A mean value of the data after normalisation of each value to pF2 and a temperature e.g. 20°C is recommended. If the available numbers of parameters is less than required by the EU Guideline (4 for parent and 3 for metabolites), then the worst case value is to be used.
According to FOCUS, the average pesticide parameters are to be used and the worst case nature of the assessment is to be associated to the soil and weather conditions. If a special relationship exists between pesticide parameters and soil properties this relation has to be taken into account to achieve the realistic worst case assessment of the regulatory endpoint.

At tier 1, FOCUS GW guideline recommends to use mean value of K_{oc}/K_{om} data and a 1/n according to experimental data; if 1/n is not available default value for 1/n = 0.9.
When characterising sorption behaviour of ionic compounds, the value will vary depending on the pH and a mean or median value is no longer appropriate. In this situation it is recommended that the choice of input parameter is made in relation to the pH of the soils in the scenario in the first instance.

Q No.	Question	National Approach
16	**Half-life (DT50)**	

16.1	Half-life (DT50), <u>at tier 1</u>, how do you choose half-life
	a) Do you use lab or field data?
	b) Do you normalise data according to FOCUS recommendations?
	c) How do you treat your data before input into the model?
	d) How do you consider pH dependency of degradation, if this can be identified from the data?
		a) State which
		b) Yes
		   No
		c) Arithmetic mean value
		   Geometric mean value
		   Median value
		   Worst case
		   A specific percentile, which
		d) Specify

16.2	Half-life (DT50), <u>at higher tiers</u>
	
	a) Do you use lab or field data?
	b) Do you normalise data according to FOCUS recommendations?
	c) How do you treat your data before input into the model?
	d) Do you consider half-lives from specific soils (e.g. lysimeters, use areas of the compound, special properties like pH) of higher relevancy?
	e) Do you consider half-lives from specific study types (e.g. lysimeter, micro-lysimeter) of greater relevancy?
		a) State which
		
		b) Yes
		   No
		c) Arithmetic mean value
		   Geometric mean value
		   Median value
		   Worst case
		   A specific percentile, which
		
		d) Yes,
		   No,
		   If yes, which criteria do you consider?
		
		e) Yes,
		   No,
		   if yes, which study types do you consider?

Q No.	Question	National Approach
17	Sorption data	
17.1	Sorption <u>at tier 1</u> a) Which available experimental data do you use? b) How do you treat the data before input into the model?	a) K_{oc} (batch studies, OECD guideline 106) Time dependent sorption Other b) Arithmetic mean value Geometric mean value Median value Worst case A specific percentile, which
17.2	Sorption data <u>at higher tier</u> a) Which available experimental data do you use? b) How do you treat the data before input into the model? Do you consider specific sorption experiments and sorption evaluations (e.g. long term or kinetic sorption, lysimeters, micro-lysimeters, column studies, desorption values, penetration depth in field studies)?	a) K_{oc} (batch studies, OECD guideline 106) Time dependent sorption Other b) Arithmetic mean value Geometric mean value Median value Worst case A specific percentile, which c) Yes, No, if yes explain how.
18	If you have a tiered approach in your scheme, specify the choice of parameters (sorption and/or degradation) at each step	
19	Do you apply quality criteria for experimental data?	Yes No
19.1	How does the application of quality criteria influence the regulatory decision-making	

6 Additional Experimental data

Q No.	Question	National Approach
20	Do you request further experimental data for the national assessment than is available in the EU dossier? If Yes, go to Q No. 20.1	Yes No
20.1	Which additional data do you request and what triggers the request? a) Lysimeter data b) Field leaching c) Monitoring data d) Other	a) Lysimeter Triggers: No EU lysimeter available Nat conditions differ from EU lysimeter Other reasons b) Field leaching Triggers: No EU lysimeter available Nat conditions differ from EU lysimeter Other reasons c) Monitoring data d) Other
21	Lysimeter /field leaching data	
21.1	Do you have national guidelines for lysimeter/field leaching studies?	Yes No
21.2	a) Which information do you take from lysimeter/field leaching data? b) Which endpoint do you use for parent, metabolites, not identified radioactivity?	a) b) Highest concentration (µg/l) Monthly mean Yearly mean An all over mean

Q No.	Question	National Approach		
22	Do you request or have an option for a post-registration monitoring?	Yes		
		No		
		If yes, please describe what may trigger it and what are the requirements/guidelines		

7 Interrelationship Models – Higher tier experiments

Q No.	Question	National Approach
23	Do model results override results from field studies i.e. models are considered weighted higher than e.g. lysimeters?	Yes No
24	Do results from field studies override model results i.e. lysimeters are considered weighted higher than models ?	Yes No
25	Do you jointly consider models and e.g. lysimeters/field leaching studies and take a decision based on quality of the two cases?	Yes No
26	Do you apply model calculations to extrapolate experiments to national or regional assessment?	Yes No

8 Handling of metabolites

EU Approach

In the EU metabolite guidance document (Sanco/221/2000 –rev.10), there is a tiered scheme how to identify metabolites, which are biological active or which are toxic. Metabolites defined as relevant are judged to be equivalent with active substances. For relevant metabolites the trigger value in groundwater is 0.1 µg/L.

Q No.	Question	National Approach
27	Do you define metabolites according to the EU guidance document on relevant metabolites (rev 10)?	Yes No If no, please define the criteria to classify a metabolite as relevant describe where your exposure or relevancy triggers differ from the EU approach
28	Have you set a trigger value different from parent for metabolites, relevant or non-relevant, If Yes, at what concentration?	Relevant metabolites: Yes No At concentration: Non-relevant metabolites Yes No At concentration:

APPENDIX 2. REPONSES TO THE QUESTIONNAIRE

The responses to the questionnaire are tabulated below. Entries are provided only when a response was made.

1   **Does your country assess risk to groundwater as a routine before approval of a PPP in your country?**

Denmark	Y
Germany	Y
France	Y
Ireland	Y
Italy	Y
Austria	Y
Netherlands	Y
Portugal	Y
Finland	Y
Sweden	Y
United Kingdom	Y
Czech Rep.	Y
Slovakia	Planned but not yet implemented
Slovenia	Y
Estonia	Y
Lithuania	Y
Poland	Planned but not yet implemented
Latvia	Y

2   **Is the EU GW assessment as defined in the FOCUS GW guideline sufficient for the risk assessment in the authorisation procedure of PPP in your country?**

Denmark	N
Germany	N
France	N
Ireland	Y
Italy	N
Austria	Y
Netherlands	N
Portugal	Y

Finland	N
Sweden	Y, the methodology is sufficient. Regarding the scenarios see question 10.
United Kingdom	N
Czech Rep.	Y
Slovakia	Y – under study
Slovenia	Y
Estonia	Y
Lithuania	Y
Poland	N
Latvia	Y

2.1 **State shortly the main reason/s why the FOCUS GW guideline is not sufficient.**

Denmark	The FOCUS guideline is not considered to be sufficiently protective and the scenarios not fully representative for Danish conditions
Germany	For model calculations a certain national scenario is specified. The national scenario is evaluated on the basis of lysimeter and field studies. Valid results from higher tier experimental studies (lysimeter or comparable field studies) override the modelling results in the assessment.- FOCUS input parameter guidance is not sufficient- the "one safe use" concept currently followed by the EU is not satisfying.
France	Representativity of EU FOCUS GW scenarios is not established for the French environmental conditions. EU GW assessment considered as sufficient only if all FOCUS GW scenarios are acceptable.
Italy	The nine FOCUS scenarios do not cover all the Italian territory. Moreover, major crops of Italy are not totally represented
Netherlands	Specific aquifer conditions, high ground water tables and vulnerable soils, no higher tier guidance available in the guideline
Finland	The guidelines are mainly sufficient but more detailed advice could be given for instance how many different models should be used.
United Kingdom	In the main the EU GW assessment is sufficient as defined in the FOCUS GW guideline, however for more strongly adsorbed compounds MACRO / Château dun must be used for UK national assessments, this is only an option in FOCUS GW guidelines, whilst it is a requirement for the UK.
Poland	Existing scenarios do not fully cover the whole country in terms of soil and climate conditions

2.1.1   **Which groundwater assessment schemes do you use for national risk assessment?**

Slovakia   value of DT50 and K_{oc} and GUS coefficient, results of lysimeters study, simultaneously we study GW guideline and EU evaluations process

Estonia   Tier I FOCUS (scenario Jokioinen); Tier II field/lysimeter studies, additional transformation rate (degradation kinetics) studies; higher tier expert judgement based on local conditions + monitoring data

Poland   Tiers I and II: FOCUS – at present all scenarios would be required, in future probably Hamburg, Kremsmünster (this depends on the results of work on fitting of the scenarios to our weather and pedological conditions) and, probably but not necessarily, Piacenza. Higher tiers: lysimeter/field leaching studies

Latvia   Tier 1: Hamburg and Jokioinen scenarios
Higher Tier: Lysimeter, field leaching studies and monitoring data

2.1.2   **Do you have any training for the risk assessment to groundwater in any MS?**

Czech Rep.   Yes, UK (PSD)

Slovakia   Took participation in 3 days course in Wageningen to use FOCUS_PEARL

Slovenia   UK (Holland)

Estonia   Yes, DK and NL

Lithuania   Yes, DK, (bilateral project), postgraduate training "Modelling of pesticides fate in the environment for national and EU registration" NL

Poland   Yes, UK (PSD)

Latvia   Y. UK(Twinning Light)

2.2   **In order to improve the existing Tier I FOCUS groundwater scheme, have you had any technical scientific difficulties (i.e. excluding software problems) with using the existing FOCUS groundwater scenarios? Examples might be, incorrect planting dates for scenarios, or non-inclusion of specific crops in scenarios etc. If yes, please provide a detailed documentation of the difficulties. Problems that have been solved already via new versions of the software packages, do not need to be reported.**

Denmark   Build in help/explanations would be appreciated – e.g. the Henry's low constant is not usually given in J/mol as required in PELMO. Also a simpler way to partition degradation rates between different

	metabolites/CO2 in PELMO would be helpful. In general we find it important that more scenarios that include preferential flow are developed.
Germany	No problems
Ireland	N
Italy	non-inclusion of specific crops in scenario: for example soybean is not considered in the Thiva scenario, relevant for Italy while like dry legumes are not included in Piacenza scenario
Netherlands	Scenarios for amenity use and glasshouses. Specific crop: ornamentals
Portugal	Until now we haven't used frequently the FOCUS models, we check the data presented by the notifier; input and output data.
Finland	There has been some technical problems in giving the user defined application scheme to PEARL (and thus in running the model). A possible solution is already given by FOCUS helpdesk.
Sweden	We have only limited experience with the EU scenarios and so far we have not had any difficulties
United Kingdom	N
Czech Rep.	N
Slovenia	no, while we are making evaluation for 1st year
Estonia	N
Lithuania	The experts have limited experience in modelling. The partition rate, metabolites and CO2 in PELMO is not clearly described in the guidance document and is rather difficult. Sometimes local experts have different opinion on selection of input parameters in comparison with input parameters chosen by company experts.
Poland	Right now we check the data and calculations submitted by the notifier. The main problem in the nearest future will be the not full compatibility of the existing scenarios with our pedological and climatic conditions.
Latvia	No

2.3   Do you have needs for training in FOCUS modelling?

Czech Rep.	Y
Slovakia	Y
Slovenia	Y
Estonia	Y
Lithuania	Y
Poland	Y
Latvia	Yes (additional training with MACRO could be useful)

3	What is the trigger for national assessment of risk for groundwater contamination? If other trigger than Review Report, such as a national judgement, please, answer Q No. 3.1.
Denmark	RR and other trigger
Germany	If DT50 > 21 d or K_{oc} < 500, risk to ground water has to be assessed for every application using the special national scenario (cf. Q 1).
France	Other trigger: At least one relevant EU FOCUS GW scenario not acceptable (PECgw > 0.1 µg/L).
Ireland	RR
Italy	RR
Austria	RR
Netherlands	Always national judgement according to the Dutch pesticide act
Portugal	RR
Finland	The ground water assessments included in RR and DAR are used nationally but the risks are reassessed if the use amounts or intended uses differ from those in RR and DAR or if the Jokioinen scenario is missing.
Sweden	If risk for ground water contamination is pointed out in the RR, simulation with national scenarios is always carried out. In other cases simulations are performed with a case by case approach
United Kingdom	Other trigger
Czech Rep.	According to the Review Report (RR) for the active substance
Slovakia	According to the Review Report (RR) for the active substance
Slovenia	According to the Review Report (RR) for the active substance
Estonia	According to the Review Report (RR) for the active substance
Lithuania	According to the Review Report (RR) for the active substance
Poland	According to the Review Report (RR) for the active substance
Latvia	According to the Review Report (RR) for the active substance

3.1	If the trigger is according to national criteria?
Denmark	Assessment in EU re-registration process did not result in recommendations in the RR, but "national" criteria" raise concerns that have to be addressed on MS level: Borderline assessments in the EU process and potential issues with metabolites that have not been considered relevant in the EU process. justification: We perform a stricter national assessment and consider more metabolites to be "relevant".

	Earlier national assessment prior to the EU re-registration. Positive findings from ground water monitoring data
Germany	PELMO 3.0 calculation ifDT50 > 21 d or K_{oc} < 500; lysimeter study if PELMO 3.0 results in concentrations > 0.1 µg/L; justification: Substances with properties indicating a certain mobility and persistence in soil are subject to a more detailed assessment. Field studies are higher tier studies and overwrite calculations. Positive findings from ground water monitoring data: Further information about the findings is required and further studies might be triggered.
France	Assessment in EU re-registration process did not result in recommendations in the RR, but "national" criteria" raise concerns that have to be addressed on MS level; criteria See 3; justification See 2.1
Netherlands	Always national judgement; justification: NL specific conditions as listed at question 2.1; Earlier national assessment prior to the EU re-registration Yes can be a reason as well; Positive findings from ground water monitoring data Always a reason for extra secure judgement on a national level
Portugal	Y
Finland	Y
Sweden	We have no specific criteria - case-by-case decision based on the results from the simulations with the EU-scenarios.
United Kingdom	1. GAP from UK proposed use (proposed label use pattern) must be assessed, if this is different to that assessed by the rapporteur. 2. Preferential flow must be assessed using MACRO Châteaudun for some compounds (K_{oc} >100ml/g). 1. The actual requested UK use pattern has to be assessed if it differs in any way from the 'intended supported safe use' identified as supporting the annex 1 listing decision. . More structured soils where preferential flow can be of concern that are associated with relatively vulnerable ground water aquifers are relatively common in the UK. Therefore this needs assessing.
Estonia	Assessment in EU re-registration process did not result in recommendations in the RR, but "national" criteria" raise concerns that have to be addressed on MS level. If EU re-registration process will result in FOCUS Tier I for scenario Jokioinen in leaching > 0.1 µg/L, we will apply the national RA according to our conditions. Plus positive finings from monitoring data in Nordic countries

4   Do you assess along a tiered approach?

Denmark	Y
Germany	Y
France	Y
Ireland	Y
Italy	Y
Austria	Y
Netherlands	Y
Portugal	Y
Finland	N
Sweden	Y
United Kingdom	Y
Czech Rep.	N
Slovakia	N
Slovenia	No, so far
Estonia	Y
Lithuania	Y
Poland	Y, such approach is planned.
Latvia	Yes

4.1   Briefly describe the tiered approach you apply

Denmark   First tier is based on standardised input values, second tier refines the input values and takes into account more specific issues if justified.

Germany   Consideration of the active substance's properties with regard to soil sorption and degradation. Model calculation with a national specific scenario. Higher tier experimental study (Lysimeter or comparable field studies) if modelling results indicate contamination above 0.1 µg/L

France   1- All relevant FOCUS GW scenarios acceptable. 2- If not, national approach : simulations of national scenarios with one FOCUS model (lysimeter study also taken into consideration).

Ireland   Results from the Okehampton and Kremsmünster scenarios are used in the first tier. If PEC values for active substance or relevant metabolite(s) exceed 0.1 µg/L for either of these scenarios, then a higher tier leaching assessment is required, involving, for example, a lysimeter or field leaching study conducted under vulnerable conditions appropriate for Ireland. Site-specific modelling using Irish data and Irish ground water monitoring data, if available, could also be used in higher tier national

	leaching assessments. The exact nature of the higher tier assessment is determined on a case-by-case basis.
Italy	Refined modelling; Use of document of relevancy of metabolites
Austria	Lysimeter studies are considered as higher tier studies
Netherlands	Tier 1: FOCUS Kremsmünster; Tier 2: GeoPEARL, field/lysimeter studies, extra (more relevant) lab studies, monitoring uppermost ground water. Tier 3: behaviour in the saturated zone, monitoring deeper ground water; The Dutch decision tree and the underlying steps are described in the following reports
Portugal	We follow the FOCUS Guidance document
Sweden	1) Simulations with normalised laboratory half-lives, 2) Simulations with normalised field half-lives if available, 3) Look at available EU field lysimeters and decide whether they are relevant for Swedish conditions. 4) Request of field lysimeter under Swedish climatic conditions if unacceptable leakage has been simulated and the EU field lysimeters are not considered relevant. In cases with metabolites an assessment of the relevance of the metabolite, 5) Overall assessment based on all available data.
United Kingdom	See attachment; and http://www.pesticides.gov.uk/applicant/registration_guides/data_reqs_handbook/env_fate.pdf
Estonia	Tier I FOCUS (scenario Jokioinen) ☐ Tier II field/lysimeter studies, additional transformation rate (degradation kinetics) studies ☐ higher tier expert judgement based on local conditions + monitoring data
Lithuania	First Tier modelling is based on worse case standard input values (e.g. DT50 only from lab studies), the refinement is done taking into account for refined input parameters. The results of field lysimeter studies (if studies done are relevant for local conditions) are considered higher tier
Poland	Generally: Step 1: Focus modelling using more conservative lab. degradation kinetics values, Step 2: Focus modelling using more realistic degradation kinetics values from field studies (whenever available)/opt. lysimeter or field leaching studies, Step 3: Lysimeter/field leaching studies.
Latvia	1) The use of Hamburg and Jokioinen scenarios (Jokioinen is considered as worst case). 2) Lysimeter/field studies, monitoring data from Northern parts of Europe.

5a **How do you define the endpoint value for approval? a) Tier 1**

Denmark 0.1 µg./l, defined as the 95th percentile concentration derived by FOCUS PELMO Hamburg or the Danish MACRO scenarios averaged over each year, for as and metabolites; at depth 1 m

Germany 0.1 µg/L, maximum annual average concentration at depth 1 m

France Same criteria as EU approach (with FOCUS GW as well as with national scenarios).

Ireland 80th percentile annual average concentration (or 2- or 3-year average, as appropriate) at 1 m depth must not exceed 0.1 µg/L

Italy depth 1 m

Austria depth 1 m

Netherlands <0.1 µg/L at depth 1 meter

Portugal 1 meter

Finland depth 1 m, 80th percentile annual average concentration

Sweden below root depth, 1.3-1.6 m

United Kingdom 1 m

Czech Rep. at I m depth

Slovakia at I m depth

Slovenia at I m depth

Estonia endpoint value < 0.1 µg/L for parent and for metabolites according to FOCUS Tier I GW modelling using scenario Jokioinen and DT50 lab value

Lithuania 80%-ile annual concentration at 1 m depth >0.1 µg/L (derived from FOCUS PELMO Hamburg and Jokioinen scenarios) for both AS and metabolites.

Poland <0.1 µg/L at 1 m depth

Latvia <0.1 µg/L at 1 m depth

5b **b) At higher tiers**

Denmark as tier 1

Germany 0.1 µg/L, maximum annual average concentration at depth 1 m

Ireland If it can be demonstrated that depth to ground water in areas of use is >1 m, then annual average concentration impacting on top of the ground water body must not exceed 0.1 µg/L.

Netherlands 90th percentile <0.1 µg/L at depth/s 1-10 m

Portugal to be defined

Sweden see Tier 1

United Kingdom	The depth of simulation is to that which is technically feasible. However applicants need to justify the use of the depth for which results are presented and their relationship to UK vulnerable ground water depths as associated with the intended cropping. Information on where ground water is shallow, cropping patterns and where soils are vulnerable to ground water contamination can be extracted from the latest version of the SEISMIC data base that covers England and Wales.
Estonia	endpoint value should be still < 0.1 µg/L for parent and for metabolites, using for modelling the extrapolation of data from lysimeter/field studies and considering monitoring data; if the endpoint for metabolites is > 0.1 µg/L, the toxicological relevance of metabolites is considered
Lithuania	Same as in 5a
Poland	<0.1 µg/L at 1 m depth
Latvia	<0.1 µg/L at 1 m depth

6a   **Do you apply a safety factor on the endpoint a) For parent**

Denmark	N
Germany	N
France	N
Ireland	N
Italy	N
Austria	N
Netherlands	N
Portugal	N
Finland	N
Sweden	Y, in the case of triggering a higher tier assessment
United Kingdom	N
Czech Rep.	N
Slovenia	N
Estonia	N
Lithuania	N
Poland	N
Latvia	N

6b   **b) For metabolites**

Denmark	N
Germany	N

France	N
Ireland	N
Italy	N
Austria	N
Netherlands	N
Portugal	N
Finland	N
Sweden	Y, in the case of triggering a higher tier assessment
United Kingdom	N
Czech Rep.	N
Slovenia	N
Estonia	N
Lithuania	N
Poland	N
Latvia	N

7	**Do you take decisions using model simulations only?**
Denmark	No usually not, but we might for new substances, see below
Germany	Yes, if field studies are not required according to the tiered approach. No, in all other cases
France	N; Lysimeter also considered when available.
Ireland	N, (See reply to Q.4.1)
Italy	N
Austria	N
Netherlands	N, See references mentioned at 4.1
Portugal	N
Finland	N
Sweden	N
United Kingdom	Y
Czech Rep.	N
Slovakia	N
Slovenia	Y
Estonia	N
Lithuania	Yes (Positive or negative), If modelling demonstrate leaching < 0,1µg/L , the positive decisions are based only on modelling, . If modelling demonstrates leaching > 0,1 µg/L and field lysimeter data are not

available, the negative decisions are also based only on modelling results. If field lysimeter data are available- they are considered.

Poland	N
Latvia	N

8a **Are the following possible alternatives to non-full-approval? a) Conditional approval?**

Denmark	Yes in the sense that uses are restricted e.g. max dose, max # appl., only spring/summer use etc.
Germany	Y
France	Yes, Under discussion
Ireland	Y
Italy	Y
Austria	Y
Netherlands	Yes with a demand for post registration monitoring of the uppermost ground water
Portugal	Y
Finland	Y
Sweden	Y
United Kingdom	N
Czech Rep.	Y
Slovenia	Y
Estonia	N
Lithuania	Y
Poland	Y
Latvia	N

8b **b) Regional or local approval?**

Denmark	N
Germany	N
France	Yes, Under discussion
Ireland	Y (This is possible but would not be common.)
Italy	Y
Austria	N
Netherlands	Y
Portugal	Y
Finland	N

Sweden	N
United Kingdom	N
Czech Rep.	N
Slovenia	Y
Estonia	N
Lithuania	N
Poland	N
Latvia	N

8c	**c) Special approval for farmers?**
Denmark	N
Germany	N
France	Yes, Under discussion
Ireland	Y (This is possible but in such a situation we would use the term "professional users" instead of "farmers".)
Austria	N
Netherlands	N
Portugal	Y
Finland	N
Sweden	N
United Kingdom	N
Czech Rep.	N
Estonia	N
Lithuania	N
Poland	Planned but not implemented.
Latvia	N

8d	**d) Special indications?**
Denmark	Dispensations can be granted prior to Annex 1 inclusion if the need is considered valid and the risks acceptable
Germany	in reasonable special cases approval in combination with post-authorisation monitoring is possible
France	Under discussion
Austria	Time of application
Netherlands	Ground water protection areas
Portugal	Approval conditions to type of soil/crop/agronomic conditions
Finland	N

Poland	Ground water protection areas (mainly drinking water sources)
Latvia	N

9	**Are risk mitigation measures considered at approval on your national level?**
Denmark	No Not for gw - unless you consider the above mentioned (8) restrictions to be risk mitigations
Germany	Y. E.g. restriction with regard to the soil type (no application on heavy clay soils or sand soils), restriction with regard to the maximum amount of a certain active substance to be applied to the same field in the course of one season (possibly from different plant protection products), restrictions with regard to the use on drained areas
France	Yes, Under discussion
Ireland	Y Possibility of using a reduced rate of application and/or reducing the frequency of application can be considered.
Italy	N
Austria	Y, Time of application, Reduction of application rates/number of applications per season
Netherlands	Y, Label restrictions e.g. use restricted to artificial soil (glasshouses), no autumn use.
Portugal	Y, Ex. If a compound may leach we restrict there use in sandy soils or soil of low o.m. content.
Finland	Y. Products having risks to leach in ground water (for instance model simulations > 0.1 µg/L) are not allowed to use in classified ground water areas.
Sweden	N
United Kingdom	N, not routinely. However if an applicant had a demonstrably robust mitigation that was practical to implement, then subject to its approval by the UK Advisory Committee on Pesticides and Ministerial agreement an authorisation would be possible. (Note as yet there are no practical examples where this has occurred).
Czech Rep.	Yes, if reductions in dose or number of applications are accepted by the applicant
Slovakia	If the application of formulation or dose is changed
Slovenia	Y
Estonia	Yes, Restrictions of applications on vulnerable soils or areas, restrictions of applications on consecutive years, reduction of dose rate etc.

Lithuania	Y
Poland	N
Latvia	Just in terms of application timing

10   **Do you use any of the nine FOCUS groundwater scenarios as your national scenario?**

Denmark	Y, PELMO Hamburg
Germany	N
France	N
Ireland	Y Okehampton and Kremsmünster
Italy	Y, All, but Thiva, Piacenza and Châteaudun seems to the most representative
Austria	Y, Hamburg, Kremsmünster, Piacenza
Netherlands	Y, Kremsmünster
Portugal	Y, Sevilla, Porto, Thiva , Piacenza
Finland	Y. Jokioinen scenario is used as a national scenario because our national scenario is not yet finalised.
Sweden	N
United Kingdom	Y, Hamburg, Châteaudun, Okehampton, Kremsmünster
Czech Rep.	N
Slovakia	Yes – is planned
Slovenia	Y
Estonia	Y, Jokioinen but only for Tier 1 and 2
Lithuania	Y
Poland	Y, planned. At present we would recommend all nine scenarios, in future probably Hamburg, Kremsmünster and, possibly, Piacenza.
Latvia	Y, Hamburg and Jokioinen

10.1   **If you have scenario/s different from the FOCUS GW scenarios, please, state shortly the reason to that?**

Denmark	We have two national MACRO scenarios (Karup and Langvad) that represent a sandy and a clay soil type. The scenarios represent realistic worst case representative Danish conditions and include preferential flow.
Germany	The national scenario is validated based on realistic lysimeter and field studies. No averaging over several years. - Soil scenario is very similar to FOCUS "Hamburg" but includes more realistic degradation factors for

	deeper soil layers than the commonly attributed factors in all of the FOCUS scenarios
France	To take account of more realistic conditions.
Austria	The three FOCUS scenarios mentioned above are considered as a compromise. If a company submits model calculations with specific Austrian soil and weather conditions we evaluate them and prefer them to the above mentioned FOCUS scenarios. In most cases the three FOCUS scenarios can be seen as a worst case.
Sweden	Yes. Swedish scenarios cover a colder climate in combination with relevant soil types and crops. Macro pore flow is included in the Swedish scenarios.
Slovenia	We are going into the process of establishing our own scenarios
Estonia	Jokioinen, but only Tier I and II
Poland	N
Latvia	N

11	**Do you have more than one national scenario?**
Denmark	Y, 2
Germany	N
France	Y. Pending standard national scenarios, notifier is asked to propose scenarios covering the major conditions of use.
Italy	N
Netherlands	N
Portugal	N
Finland	N
Sweden	Y, 3
United Kingdom	Yes we use the 4 FOCUS scenarios as listed in section 10 above + sometimes a MACRO simulation at Châteaudun is also required (see reply to question 4.1).
Czech Rep.	N
Slovakia	N
Slovenia	N
Estonia	N
Lithuania	N
Poland	N, none at present (but planned in future)
Latvia	We use two Focus scenarios

12a   **Which criteria are used for the choice of national scenarios? a. weather (rainfall)**

Denmark	Weather typical for major agricultural area/s
Germany	Average rainfall more or less (alternation of "Hamburg wet" 1961 and "Hamburg normal" 1978
France	Under discussion
Finland	Weather typical for major agricultural area/s
Sweden	Weather typical for major agricultural area
Slovenia	Typical for agriculture areas
Estonia	Average rainfall
Latvia	Average rainfall

12b   **b. weather (temperature)**

Denmark	Weather typical for major agricultural area/s
Germany	Average temperature more or less (alternation of "Hamburg wet" 1961 and "Hamburg normal" 1978)
France	Under discussion
Finland	Weather typical for major agricultural area/s
Sweden	Weather typical for major agricultural area
Slovenia	Typical for agriculture areas
Estonia	Average temperature
Latvia	Average temperature

12c   **soil type**

Denmark	Worst case soil + realistic and representative
Germany	realistic worst case soil
France	Under discussion
Finland	Worst case soil
Sweden	Soil/s typical for major agricultural area
Slovenia	Typical for agriculture areas
Estonia	Typical for major agricultural areas
Latvia	Soils typical of major agricultural area/s

12d   **crops**

Denmark	Crops in general
Germany	Crops according to the GAP for which authorisation is sought
France	Under discussion

Finland	Crops typical for major agricultural area/s
Sweden	Crops typical for major agricultural area
Slovenia	Crops in general
Estonia	Crops in general
Latvia	Crops typical of major agricultural areas

12e **In defining a scenarios is any of a) to d) more important than the other?**

Italy	a) and d)
Netherlands	Kremsmünster scenario based on comparison between NL old and EU scenarios, important is fluctuating ground water table. See report on decision tree
Slovenia	rainfall and soil properties
Estonia	Temperature
Latvia	None

13 **Do you consider your scenario/s more or less conservative than the 9 FOCUS scenarios?**

Denmark	More in general, however the Hamburg scenario gives very similar results to the Karup scenario and is therefore accepted
Germany	Other. No direct comparison and therefore no short answer possible. Our national scenario is similar to the FOCUS scenario Hamburg, but it is less conservative than the FOCUS scenario Piacenza and more conservative than the FOCUS scenarios Thiva and Sevilla.
Netherlands	equal
Finland	More
Sweden	More, Slightly more conservative since macropore flow is considered
Latvia	Not applicable

14 **Do you consider your national scenarios as higher tier compared to FOCUS Tier 1?**

Denmark	Y, the Danish scenarios are based on actual sites (that are experimentally parameterised), soil types, climate etc. are therefore more representative and relevant for national approvals.
Germany	N
France	Y. More realistic
Austria	Y, See point 10.1

Netherlands	No, equal at Tier 1
Finland	N
Sweden	Y, More representative for Swedish conditions
Estonia	Yes, the extrapolation of data from lysimeter/field studies is used, expert judgement according to local conditions and considering vulnerable areas and soils

15	**Do you have a requirement to special model/s?**
Denmark	Yes ? In principle, but other models are accepted in some cases (e.g. PELMO for the Hamburg scenario)
Germany	Y, PELMO 3.0, Using the national scenario, a conservative estimation of possible leaching to ground water is obtained, which was evidenced by comparison with the results of lysimeter and field leaching studies.
France	Yes ? One of the 4 FOCUS GW models
Ireland	N
Netherlands	No, but same circumstances as PEARL (dispersion length!)
Portugal	Y, PELMO (PEARL)
Finland	No
Sweden	Y, Swedish scenarios use MACRO in FOCUS. Need of model that can handle macro pore flow
United Kingdom	No except for compounds with K_{oc} >100ml/g, MACRO must be run for Châteaudun
Slovenia	N
Estonia	Yes, Recommended FOCUS GW models; According to national legislation
Poland	No, however if calculations using PRZM are submitted the Notifier would be asked to recalculate the PEC values using PELMO or/and PEARL.
Latvia	N

15.1	**Do you have a preference to special model?**
Denmark	MACRO, In order to include preferential flow + see attachment on modelling for details
Germany	see answer to question 15
France	N
Ireland	N
Austria	PELMO
Netherlands	PEARL! Coupled with GeoPEARL
Portugal	Y, PELMO (PEARL)

Finland	PELMO and PRZM are preferred since these models take into account that the water comes as snow during the winter time and smells gradually. The situation resembles more the natural situation in Finland
Czech Rep.	N
Slovakia	N
Slovenia	We are working with PEARL but in future we are also interested for adoption of MACRO model for specific occasions
Estonia	Yes, PEARL
Lithuania	PELMO or PEARL
Latvia	PELMO

16.1a   Half-life (DT50), at tier 1, how do you choose half-life a) Do you use lab or field data?

Denmark	laboratory data
Germany	laboratory data
France	Both are accepted (expert judgement)
Ireland	Both lab and field data can be used in the first tier but lab data is preferred.
Italy	Lab
Austria	Case by case decision
Netherlands	Lab data
Portugal	At the moment we don't use the models, however we request that modelling presented by companies follows FOCUS Guidance recommendations
Finland	Mainly lab data. Field data is used when photolysis has an important role in degradation.
Sweden	Lab data
United Kingdom	Either is appropriate providing a justification is provided and it is scientifically defendable
Czech Rep.	Lab or field possible
Slovakia	Lab
Slovenia	usually lab
Estonia	lab data
Lithuania	DT 50 lab
Poland	Usually lab. data, although the field data are also acceptable.
Latvia	Both cases are applicable

16.1b   b) Do you normalise data according to FOCUS recommendations?

Denmark	Y
Germany	Yes, but only for temperature; for moisture the value is 40 % MWHC (this is in many cases comparable to FOCUS recommendations but not always)
France	Yes Normalisation accepted
Ireland	Y (for lab data)
Italy	Y
Austria	Y
Netherlands	No, i.e. if laboratory values are at standard conditions, otherwise correction to 20ºC
Finland	Y
Sweden	Y
United Kingdom	Y
Czech Rep.	Y
Slovakia	Y
Slovenia	Y
Estonia	Y
Lithuania	Y
Poland	Y
Latvia	Y

16.1c   **c) How do you treat your data before input into the model?**

Denmark	A specific percentile, which 80th
Germany	Geometric mean value, median value or worst case of degradation rates, depending on number of values and their variability
France	Arithmetic mean value, geometric mean value, median value, a specific percentile is under discussion
Ireland	Generally arithmetic mean value is used but median or geometric mean may be appropriate in some cases, depending on the distribution of the data.
Italy	Arithmetic mean/median
Austria	Arithmetic mean/median, the higher value of these two
Netherlands	Arithmetic mean; geometric mean; median value only with more than 10 values or >/< values
Finland	Arithmetic mean value
Sweden	Arithmetic mean
United Kingdom	Geometric mean value; median value if data set is large
Czech Rep.	Geometric mean value; median value

Slovakia	Geometric mean value; worst case
Slovenia	Arithmetic mean value; median value
Estonia	Arithmetic mean value
Lithuania	Arithmetic mean value, worst case
Poland	Arithmetic mean value
Latvia	Geometric mean; median value

16.1d   **d) How do you consider pH dependency of degradation, if this can be identified from the data?**

Denmark	Not considered at tier 1, can be considered at tier 2 when refining input values
Germany	Use of realistic worst case data instead of mean
France	Values selected according to realistic pH range
Ireland	Preference is for a regression equation showing the correlation between soil pH and degradation but can also model alkaline and acidic soils separately, using average alkaline degradation value and average acidic degradation value, respectively
Austria	Take the half life which covers best Austrian soils
Netherlands	if adequate data is available it is considered
Finland	When using Jokioinen as national scenario, the degradation value is taken from the soil that has pH value most close with Jokioinen (acid values are used since fields in Finland are acidic).
Sweden	use geometric mean from soils with relevant pH if the number of values is sufficient. In other cases use worst-case value
United Kingdom	Expect applicant to use the worst case DT50 from the pH conditions that could be tolerated by the crop on which use is requested
Czech Rep.	DT50 acidic/DT50 alkaline soils
Slovakia	with Calcstuff from other EU member – Arrhenius correction
Slovenia	As a separate case for each pH condition, which can lead to conditional approval
Estonia	input parameter will be selected in the relation to the representative soil pH
Lithuania	At first tier it is not considered
Poland	Not considered at Tier 1
Latvia	Use worst case at Tier 1

16.2a   **Half-life (DT50), at higher tiers a) Do you use lab or field data?**

Denmark	lab or field if justified more relevant for Danish conditions/uses

Germany	Use of field data possible.
Ireland	Both (no specific preference at higher tiers, other than that it can be demonstrated that the data are appropriate for Ireland).
Austria	Field data
Netherlands	both can be used. Field data if according to checklist Dutch authorisation manual
Portugal	At the moment we don't use the models
Finland	Field data, see above
Sweden	field data
United Kingdom	Either is appropriate providing a justification is provided and it is scientifically defendable
Slovenia	field, sometimes lab
Estonia	field data
Lithuania	DT50 lab and DT50 field
Poland	on this stage rather field data (if available)
Latvia	Field

16.2b   b) Do you normalise data according to FOCUS recommendations?

Denmark	Y
Germany	Yes, Normalisation possible, but not in all cases. Normalisation on a daily basis is recommended (FOCUS report does not recommend a normalisation procedure for field data)
Ireland	Y (for lab data).
Italy	Y
Netherlands	Y
Finland	Y
Sweden	Y
United Kingdom	Y
Slovenia	Yes, if we use lab data
Estonia	Y
Lithuania	Y
Poland	Y
Latvia	Y

16.2c   c) How do you treat your data before input into the model?

| Denmark | A specific percentile, which 80th |

Germany	Geometric mean value, median value or worst case of degradation rates, depending on number of values and their variability
Ireland	Generally arithmetic mean value is used but median or geometric mean may be appropriate in some cases, depending on the distribution of the data.)
Italy	median
Netherlands	Arithmetic mean; geometric mean; Median value only with more than 10 values or >/< values
Sweden	Arithmetic mean
United Kingdom	Geometric mean value; median value, generally however if the applicant proposed something different if defendable it could be accepted
Slovenia	Arithmetic mean value; median value
Estonia	Arithmetic mean value; worst Case
Lithuania	Arithmetic mean value, worst case
Poland	Arithmetic mean value
Latvia	Geometric mean or median value

16.2d   d) Do you consider half-lives from specific soils (e.g. lysimeters, use areas of the compound, special properties like pH) of higher relevancy?

Denmark	Yes, Relevance for Danish conditions/uses based on expert judgement
Germany	No, Exceptions in specific cases may be possible
France	Yes, For use areas of the compound Y
Ireland	Y, It is preferable if K_{oc} values for the specific soils are available in addition to the half-life values. An indication is required of how appropriate data from specific soils are for Ireland (e.g. a GIS analysis would be helpful).
Italy	Y
Netherlands	Y, If adequate data is available these are considered in Tier 2
Finland	Yes, Use areas of the compound, pH dependency
Sweden	N
United Kingdom	No, not usually but any proposal that this was the case by the applicant, that stood up to independent scientific scrutiny and was pertinent to the intended use would be accepted
Slovenia	Yes, Depends on a.s
Estonia	Yes; Lysimeters, use area of the compound
Lithuania	N

Poland	N
Latvia	N

16.2e	**e) Do you consider half-lives from specific study types (e.g. lysimeter, micro-lysimeter) of greater relevancy?**
Denmark	No, only if these are more relevant for Danish conditions/uses
Germany	N
France	N
Ireland	Y, Lysimeter, field leaching and saturated zone studies can all be considered, particularly if their relevancy to Irish conditions is demonstrated
Italy	Y, lysimeter
Netherlands	N
Sweden	N
United Kingdom	No, we have no preference for particular study types, however we would consider data from other study types as long as the applicant had a valid justification for why they were more pertinent. Particular scrutiny would be made of the way the data from novel study designs was used as input to the modelling to ensure that simulations would remain valid and that processes were not being double counted.
Slovenia	NY
Estonia	Yes, Lysimeters
Lithuania	N
Poland	N
Latvia	N

17.1a	**Sorption at tier 1 a) Which available experimental data do you use?**
Denmark	K_{oc} (batch studies, OECD guideline 106), Time dependent sorption
Germany	K_{oc}
France	K_{oc} (batch studies, OECD guideline 106)
Ireland	K_{oc}
Italy	K_{oc}
Austria	K_{oc}
Netherlands	K_{oc}, column leaching OECD 312 (low K_{oc} and/or fast degradation)
Portugal	K_{oc}
Finland	K_{oc} (batch studies, OECD guideline 106
Sweden	K_{oc}

United Kingdom	K_{oc}
Czech Rep.	K_{oc} (batch studies, OECD guideline 106); Time dependent sorption
Slovenia	K_{oc} (batch studies, OECD guideline 106)
Estonia	K_{oc} (batch studies, OECD guideline 106)
Lithuania	K_{oc} (batch studies, OECD guideline 106)
Poland	K_{oc} (batch studies, OECD guideline 106)
Latvia	K_{oc} (batch studies, OECD guideline 106)

17.1b   **b) How do you treat the data before input into the model?**

Denmark	A specific percentile, which 80th
Germany	Arithmetic mean value, (depends on number of values) if correlation to organic carbon content is > 0.7 ; if correlation to organic carbon content is < 0.7 and dependency on other soil parameters (clay, CEC or pH) exists, horizon-specific K_f-values are used directly in the model
France	Arithmetic mean value, Geometric mean value, Median value, A specific percentile, is Under discussion
Ireland	arithmetic mean
Italy	Arithmetic mean/median
Austria	Arithmetic mean/median, The lower value of these two
Netherlands	Arithmetic mean; geometric mean; Median value only with more than 10 values or >/< values; 1/n = 0.9 with n=4
Portugal	At the moment we don't use the models
Finland	Arithmetic mean value
Sweden	Arithmetic mean
United Kingdom	Arithmetic mean value except if pH dependence; Median value for a large dataset except if pH dependence Y
Czech Rep.	Arithmetic mean value except if pH dependence
Slovakia	Arithmetic mean value
Slovenia	Arithmetic mean value; median value
Estonia	Arithmetic mean value
Lithuania	Arithmetic mean value, worst case
Poland	Arithmetic mean value
Latvia	Arithmetic mean value

17.2a   **Sorption data at higher tier a) Which available experimental data do you use?**

Denmark	K_{oc} (batch studies, OECD guideline 106), Time dependent sorption

Germany	K_{oc}
Ireland	K_{oc}
Italy	K_{oc}
Netherlands	K_{oc}
Portugal	K_{oc}
Sweden	K_{oc}
United Kingdom	K_{oc}, Time dependent sorption
Slovenia	K_{oc} (batch studies, OECD guideline 106)
Estonia	K_{oc} (batch studies, OECD guideline 106), Time dependent sorption
Lithuania	K_{oc} (batch studies, OECD guideline 106), Time dependent sorption
Poland	K_{oc} (batch studies, OECD guideline 106)
Latvia	K_{oc} (batch studies, OECD guideline 106)

17.2b　　**b) How do you treat the data before input into the model?**

Denmark	A specific percentile, which 80th
Germany	b) Arithmetic mean value (depends on number of values), if correlation to organic carbon content is ☐ 0.7; if correlation to organic carbon content is < 0.7 and dependency on other soil parameters (clay, CEC or pH) exists, horizon-specific K_f-values are used directly in the model
Ireland	arithmetic mean
Italy	median
Netherlands	Arithmetic mean; geometric mean; Median value only with more than 10 values or >/< values
Portugal	At the moment we don't use the models
Sweden	Arithmetic mean
United Kingdom	Arithmetic mean value except if pH dependence; Median value for a large dataset except if pH dependence
Slovenia	Arithmetic mean value; median value
Estonia	Worst case
Lithuania	Arithmetic mean value , worst case
Poland	Arithmetic mean value
Latvia	Arithmetic mean value

17.2c　　**Do you consider specific sorption experiments and sorption evaluations (e.g. long term or kinetic sorption, lysimeters, micro-lysimeters, column studies, desorption values, penetration depth in field studies)?**

Denmark	Yes, in principle; Not much practical experience, based on expert judgement
Germany	Y, Lysimeter study is triggered, if modelling result indicates concentration above 0.1 µg/L.
France	N
Ireland	Y, Can be considered on a case-by-case basis.
Netherlands	Y, Column studies, kinetic sorption. For 1/n mean of data is taken if more than the standard 4 values are available.
Portugal	N
Sweden	N
United Kingdom	Y, we will critically assess and scientifically scrutinise whatever the applicant proposes / supplies to support the assessment
Slovenia	Yes, As a factors in overall assessment
Estonia	Yes, Desorption values will be taken into account
Lithuania	N
Poland	N
Latvia	N

18	**If you have a tiered approach in your scheme, specify the choice of parameters (sorption and/or degradation) at each step**
Denmark	See above
France	Same approach for FOCUS GW and national scenarios
Netherlands	Tier 1 avg values for sorption and degradation, Tier 2 refinement possible upon request and available data that demonstrate necessity
Portugal	We don't have a specific tiered approach
United Kingdom	he UK tiered approach is not prescribed in this much detail. Applicants are left to make judgement on how many parameters higher tier information is required to demonstrate use is acceptable. If PSD consider the approach taken by the applicant is inappropriate or unclear it will be challenged. The applicant will be expected to justify why they consider what they have done is appropriate. Of course PSD may choose not to accept the justification provided if they consider it does not stand up to scientific scrutiny.
Lithuania	1 tier : DT50 lab, sorption not time dependent; 2 tier: DT50 lab and field, in some cases- time dependent sorption
Poland	The system is still under the development, it requires some refinements, thus it is difficult right now to fully describe it.

19   Do you apply quality criteria for experimental data??

Denmark   Yes, see attachment on assessment of field data

Germany   Y

France   Yes Expert judgement, but no specific guide

Ireland   Y

Italy   Y

Austria   Y

Netherlands   Yes Manual, report 679101022, RIVM 1995

Portugal   Y

Finland   Y

Sweden   Y

United Kingdom Yes any data that are considered unreliable upon evaluation would be excluded and not used in the model input (they would not be relied on in any other part of the exposure / risk assessment procedure either). Y

Czech Rep.   Y

Slovenia   Y

Estonia   Y

Poland   Y, expert judgement, no specific guidance.

Latvia   Y

19.1   How does the application of quality criteria influence the regulatory decision-making?

Denmark   No general answer can be given to this, will depend on the case and which data are accepted and which not based on the quality of the studies. In addition data needs to be relevant for Danish conditions which compared to the EU assessment might lead to a stricter assessment than at the EU level (e.g. due to climatic conditions)

Germany   All data assessed to be non-valid or not applicable, will be excluded from further evaluation. e.g. a K_{oc} value would be not applicable, if it was measured on a soil with < 0.3 % o.c.   DT50 values from laboratory studies might be not applicable if measured under extreme conditions (volcanic ash soil, extremely high and unrealistic application rates etc). CTB gives a useful checklist for quality criteria for field studies which is also used in Germany: "Checklist for assessing whether a field study on pesticide persistence in soil can be used to estimate transformation rate in soil." In: Appendix 3 'Field studies into rate of degradation' of Chapter 'Leaching to

	groundwater' of Authorisation manual Plant Protection Products (HTB 0.2). Document at www.ctb-wageningen.nl
Ireland	Experimental data should be obtained in a GLP-compliant facility using an appropriate guideline. Non-guideline, non-GLP studies may be accepted in some cases if it can be demonstrated that they are scientifically valid.
Italy	Rejection of data and request of new ones
Austria	Bad quality data are not considered. New data have to be submitted. In a case by case decision a time limited authorisation can be granted.
Netherlands	Studies of minor quality are excluded
Portugal	We chose preferably studies with GLP and conducted according to OECD or EU Guidelines
Finland	If the experimental data is not considered properly obtained (studies not performed according to guidelines or otherwise do not fulfil scientific validity criteria) the results are not used in decision making
Sweden	The assessment should be transparent and based on studies of acceptable quality.
United Kingdom	Yes, if excluding unreliable data means data requirements for number of studies is not fulfilled then authorisation would probably not be possible. Decision making would also be impacted if excluding data considered unreliable meant the predicted concentrations fell on a different side of the regulatory trigger/s.
Czech Rep.	If excluding unreliable data means data requirements for number of studies is not fulfilled then authorisation would probably not be possible. Decision making would also be impacted if excluding data considered unreliable meant the predicted concentrations fell on a different side of the regulatory trigger/s.
Slovenia	When the results of studies without GLP varies a lot from average of other studies than we exclude the results from overall assessment
Estonia	Decision-making is based only on experimental data obtained from studies corresponding to quality criteria
Latvia	Data of poor quality or not relevant climatic conditions are excluded from further assessment.

20	**Do you request further experimental data for the national assessment than is available in the EU dossier?**
Denmark	Y and N - If a safe use for Danish conditions/uses can not be identified based on the EU data approval is not granted. Thus we do not request

	specific data, but leave it to the applicant to submit further data to show safe use.
Germany	Y
France	Usually not, but case by case requirement possible.
Ireland	Y (if a substance fails either the Okehampton scenario or the Kremsmünster scenario).
Italy	Y
Austria	Y
Netherlands	No If tier 1 value >0.1 µg/L different options are available see 20.1
Portugal	Y, it depends on the assessment made in the EU dossier
Finland	N
Sweden	Y
United Kingdom	Yes not routinely but we can. Further experimental data would only be requested if the information in the EU dossier did not encompass UK uses and or geoclimatic conditions
Czech Rep.	N
Slovakia	N
Slovenia	N, so far
Estonia	Y
Lithuania	Further data are not routinely requested unless there were recommendations in EU dossier
Poland	Y
Latvia	N

20.1a	**Which additional data do you request and what triggers the request?** **a) Lysimeter data**
Denmark	Y, See attachment on field studies assessment
Germany	Y, if Modelling result with the national scenario indicates contamination above 0.1 µg/L
France	Case by case (a-b-c-d)
Ireland	Y - if no EU lysimeter available or national conditions differ from EU lysimeter
Austria	Y, If model calculations for Hamburg, Kremsmünster or Piacenza are shown not to be safe.
Netherlands	Y
Portugal	Y, if the concentration in ground water is > 0.1 µg/L
Sweden	Y, No EU lysimeter available, National conditions differ from EU lysimeter

| Estonia | Y, national conditions differ from EU lysimeter |
| Poland | Y |

20.1b   **b) Field leaching**

Denmark	Y, See attachment on field studies assessment
Germany	Y (may be performed instead of a lysimeter study, if quality and conditions of the study are adequate), if Modelling result with the national scenario indicates contamination above 0.1 µg/L
France	Case by case (a-b-c-d)
Ireland	Y (Generally not requested but if a relevant field leaching study was available it would be considered.)
Italy	Y
Netherlands	Y
Portugal	Y, if the concentration in ground water is > 0.1 µg/L, National conditions differ from EU lysimeter
Estonia	Y, national conditions differ from EU lysimeter
Poland	Y

20.1c   **c) Monitoring data**

Denmark	Y, See attachment on field studies assessment
Germany	results from routine controls are used as supplementary information; a tailored monitoring might be required on a case by case basis
France	Case by case (a-b-c-d)
Ireland	Y (if available)
Italy	Y
Netherlands	Y
Portugal	Y
Poland	Y

20.1d   **d) Other**

Denmark	Experimental data for metabolites or a.s. that can be used to refine input values for model calculations.
France	Case by case (a-b-c-d)
Netherlands	GeoPEARL in combination with specific data, saturated zone
United Kingdom	If the first tier modelling shows there is a concern then it is up to the applicant to provide higher tier data to demonstrate uses are acceptable. They can choose to do this by referring to an available EU lysimeter or

providing additional field data. To provide reassurance for the UK, the notifier needs to demonstrate that the conditions of the study/ies encompass UK geoclimatic conditions, cropping practice and requested uses.

21.1   **Do you have national guidelines for lysimeter/field leaching studies?**

Denmark	N
Germany	Y
France	N
Ireland	N
Italy	N
Austria	N
Netherlands	Y
Portugal	N
Finland	N
Sweden	N
United Kingdom	N
Czech Rep.	N
Slovakia	N
Slovenia	N
Estonia	N
Lithuania	N
Poland	N
Latvia	N

21.2a   **a) Which information do you take from lysimeter/field leaching data?**

Denmark	All relevant info – see also attachment on field studies
Germany	Entry of active substance or metabolites into ground water (defined by the concentration in the leachates).
France	Concentrations of compounds in drainage water and soil residues at termination in lysimeter study.
Ireland	Characterisation of leachate radioactivity, leachate concentrations, distribution and characterisation of radioactivity in the soil profile, leachate volumes.
Italy	Metabolites and concentration
Austria	Concentrations of parent and metabolites in leachates. Are the same metabolites found in the lysimeter study as in the soil metabolism and

degradation studies? Are there not-identified fractions in the leachates? Distribution of parent and metabolites within the soil core.

Netherlands	Aeric mass leached
Portugal	The edafoclimatic conditions of the study, nº of applications, application rates, %AR in the leachate and nature of AR and AR in the top soil.
Finland	Degradation rate; formed metabolites, metabolites found in leachate, K_{oc}-value
Sweden	Information about GAP, precipitation, percolation volume, total radioactivity in leachate (represented as parent and metabolites)
United Kingdom	Apart from annual average concentrations, The other key value assessed in these studies are: application rate, application timing, crop planting and harvest dates, description of the soil profile (pH, mineral texture / oc content with depth), soil temperature and recharge values for water volumes leaving the upper 1-2.5m or deeper depending on the study design. Practical issues relating to suction cup samplers are also critical when considering the results from field leaching studies.
Czech Rep.	annual average concentrations
Slovakia	average concentration (annual)
Slovenia	mobility, concentration in leachate, Y
Estonia	endpoints, DT50, adsorption/desorption, soil parameters
Lithuania	The concentration of as and metabolite in leachate. The precipitation, temperature, soil properties are also taken into account.
Poland	Information about the application, weather conditions, concentrations in the leachates
Latvia	Amount of parent and metabolites in leachate

21.2b **b) Which endpoint do you use for parent, metabolites, not identified radioactivity?**

Denmark	Yearly mean
Germany	Yearly mean concentration in the leachate at 1 m depth (lysimeter); Case-by-case assessment on basis of concentration, frequency and distribution of findings (field leaching study)
France	Highest concentration (µg/L). Yearly mean Used for decision making. Y
Ireland	Yearly mean
Italy	Highest concentration
Austria	Yearly mean

Netherlands	Highest concentration , standardisation to 90th percentile in area of use in 50th percentile of time
Portugal	Yearly mean
Finland	Yearly mean
Sweden	Highest concentration; Yearly mean
United Kingdom	Yearly mean. However the yearly mean is more complicated to estimate from field leaching studies. In the absence of the applicant having provided the information needed to calculate annual average concentrations in field leaching studies, as a worst case maximum concentrations from soil water samples would be used to support decision making.
Czech Rep.	yearly mean
Slovenia	highest concentration, all over mean
Estonia	highest concentration
Lithuania	yearly mean
Poland	highest concentration
Latvia	Yearly mean

22	**Do you request or have an option for a post-registration monitoring?**
Denmark	Y and N - We do not require this from the applicants but we do have a national monitoring system and an early warning system. Subjects for these programs are selected based on expert judgement (based on potential risk/borderline assessment, suspected misuse etc.)
Germany	Y; Trigger: Findings in ground water monitoring performed by authorities or water suppliers; Specific conditions, e.g. application on railway tracks or extrapolation of lysimeter results to different application times or crops
France	Under discussion
Ireland	Y (This is an option which could be included as a condition of authorisation but it would not be a common practice.) At present, such monitoring would only be required in exceptional circumstances and the requirements would be specific to each case.
Italy	N
Austria	Y, If at EU level it is a border line case or very critical. If positive monitoring results already found in Austria. Austrian monitoring program.
Netherlands	Y, If 90th percentile >0.1 µg/L monitoring of the uppermost ground water (Cornelese et al 2003)

Portugal	Y, We ask for monitoring data from areas were the PP will be used. In cases were there is an identified potential for leaching
Finland	N
Sweden	No, but we are planning to introduce this. In cases with contradicting results there is a need to follow up the decision.
United Kingdom	Yes, although in recent years few examples of it being used. Requirements and study protocols are agreed between the notifier and PSD, and would differ depending on the exact nature of the issue that required addressing.
Czech Rep.	N
Slovenia	Y, guideline is in the process of final definition
Estonia	N
Lithuania	Y, but in especially rare cases. Y
Poland	N
Latvia	N

23   **Do model results override results from field studies i.e. models are considered weighted higher than e.g. lysimeters?**

Denmark	N
Germany	N
France	N
Ireland	N (If model results are satisfactory, field studies are not required.)
Italy	Y
Austria	N
Netherlands	N, in general but equal in Tier 2
Portugal	Regarding this question we don't have sufficient data to answer Yes or No
Finland	N
Sweden	No all available information is considered
United Kingdom	No not automatically but depending on the situation they could
Czech Rep.	N
Slovenia	N, if the field or lysimeter studies meet appropriate requirements
Estonia	N
Lithuania	N, but it depends on studies (relevance to local conditions). If studies are done in non relevant conditions, the model results might be considered as more relevant.
Poland	N
Latvia	N

24   **Do results from field studies override model results i.e. lysimeters are considered weighted higher than models ?**

Denmark	N
Germany	Y
France	N
Ireland	Y
Italy	N
Austria	Y
Netherlands	Y, in general but equal in Tier 2
Portugal	Regarding this question we don't have sufficient data to answer Yes or No
Finland	Y
Sweden	Yes a Swedish lysimeter is considered as a higher tier
United Kingdom	No not automatically but depending on the situation they could
Czech Rep.	Y, not automatically but in cases where the application was under realistic and recommended conditions
Slovenia	Y, if the field or lysimeter studies meet appropriate requirements
Estonia	Y
Lithuania	Y, if conditions are relevant.
Poland	Y
Latvia	Y, but not always

25   **Do you jointly consider models and e.g. lysimeters/field leaching studies and take a decision based on quality of the two cases?**

Denmark	Yes Quality and how representative the cases are. Y
Germany	N, (of course, the quality of the studies has to be assessed)
France	Y
Ireland	Y (Comparability of modelling and field study results is assessed.)
Italy	Y
Austria	Y
Netherlands	Y
Portugal	Y
Finland	Y
Sweden	Y
United Kingdom	Yes, the key criteria that would affect which of the two, greater reliance would be placed would be the comparability of the approaches used to UK cropping practice and geoclimatic conditions. Modelling calibrated against

a field study, then extrapolated to the pertinent UK conditions through further modelling has been used to support UK authorisations, when the approach used best experimental and modelling practice, was adequately documented and stood up to independent scrutiny.

Czech Rep.	Y
Slovenia	Y
Estonia	Y
Lithuania	Y
Poland	Y
Latvia	Y

26   Do you apply model calculations to extrapolate experiments to national or regional assessment?

Denmark	Y
Germany	N
France	Usually no, but could be considered case by case.
Ireland	N (If model results are satisfactory, field studies are not required.)
Italy	Y
Austria	N
Netherlands	Y
Portugal	N
Finland	N
Sweden	N
United Kingdom	No, PSD doesn't but we would accept this approach if proposed by an applicant and the approach they had used followed best experimental and modelling practice, was adequately documented and stood up to independent scrutiny.
Czech Rep.	N
Slovenia	N, not yet
Estonia	Y
Lithuania	N
Poland	N
Latvia	N

27   Do you define metabolites according to the EU guidance document on relevant metabolites (rev 10)?

Denmark	N. We consider all metabolites to be relevant unless they are inherently non-problematic (e.g. CO_2, glucose, aminoacids etc.)
Germany	N; In principle, the approach is accepted. There are a few deviations and more detailed criteria have been published recently (Nachrichtenbl. Deut. Pflanzenschutzd. 56 (3), S. 53-59, 2004). A publication was issued giving more details e.g. - the exposure assessment is performed as stated above. - for the assessment of pesticidal activity specification with regard to experimental approach and trigger values (metabolite is regarded as relevant if > 30 % effect in screening test compared to the untreated control or if LC_{50} is < 3 times LC_{50} of the parent. - regarding the evaluation of toxicity it is stated that additional animal experiments with the metabolite are not required if the metabolite was found in the metabolism study with the parent. In this case classification of the metabolite can be attributed on the basis of parent data. Metabolites are relevant if T, T+ or Xn (in combination with R40, R62, R63). For metabolites not assessed to be relevant, exceeding of 0.75 µg/L will not be acceptable if the metabolite is classified as Xn.
France	Y
Ireland	Y
Italy	Y
Austria	Y, The definition of metabolites from a technical point of view is made according to the Guidance Document. The current legal situation in Austria however does not provide a distinction between relevant and non-relevant metabolites according to the Guidance Document. Discussions are still ongoing.
Netherlands	Y
Portugal	Y
Finland	No, At this moment the same criteria are applied for relevant as well as for non-relevant metabolites. However, we have discussions on going whether relevant and non-relevant metabolites should be considered differentially. The use of a product is not allowed in classified ground water areas also if a non-relevant metabolite may leach into ground water at a concentration over 0.1 µg/L.
Sweden	Y, but the guidance document will be discussed with the Swedish authority responsible for ground water
United Kingdom	Yes usually. The exception would be when a metabolite would be expected to be at or below the concentration resulting from a use identified

as a safe use for annex 1 listing, and the annex 1 listing concluded the metabolite was not relevant, but the criteria used to agree non relevance by member states for that active substance, predated the rev 10 guidance document.

Czech Rep.	Y
Slovenia	Y
Estonia	Y
Lithuania	Y
Poland	Y
Latvia	Y

28a   **Have you set a trigger value different from parent for relevant metabolites? If Yes, at what concentration?**

Denmark	N
Germany	N
France	N
Ireland	N
Italy	N
Austria	N
Netherlands	N
Portugal	N
Finland	N
Sweden	N
United Kingdom	N
Czech Rep.	N
Slovenia	Y, 0.1 µg/L (=N)
Estonia	N
Lithuania	N
Poland	N
Latvia	N

28b   **Non-relevant metabolites**

Denmark	N
Germany	Y, Similar to the EU guidance document: 0.75 µg/L ("threshold of concern" approach), general upper limit of 10 µg/L
France	N; Non-relevant metabolites (Assessed according to the EU guidance document)

Ireland	Y (0.1 µg/L threshold limit does not apply to non-relevant metabolites. A human health risk assessment should be performed to demonstrate that there are no adverse effects arising from the predicted level of exposure.)
Italy	At concentration: as suggested by the guidance on metabolite
Austria	N
Netherlands	For higher Tier studies there is no guidance for metabolites. Guidance required!
Finland	N
Sweden	N, but might change after discussion with the ground water authority
United Kingdom	Y, For parent and relevant metabolites the trigger value is 0.1µg/L. As in the rev10 guidance document for non relevant metabolites (as defined by the guidance document) concentrations up to 10µg/L would be considered acceptable. Concentrations above this might be considered acceptable, but UK Government Ministers would probably want the advice of the UK Advisory Committee on Pesticides and consultation across a wide range of UK Government Departments before uses where this occurred were authorised. There are currently no practical examples where reassessment following annex 1 listing has indicated a non relevant metabolite with a concentration of >10µg/L.
Czech Rep.	Y, according to rev. 10 guidance, up to 10 µg/L
Slovenia	N
Lithuania	N; The relevance of metabolites and 1-3 stages hazard assessment are done according to guidance document on relevance of metabolites (Sanco/221/2000-rev. 10).
Poland	N
Latvia	According to guidance doc. On the assessment of the relevance of metabolites in gw. (SANCO/221/2000-rev.10)

APPENDIX 3. FOCUS GROUND WATER STUDY INFORMATION TABLES

Study, Directive OECD Number	Description	Useful information
Aerobic soil degradation (Laboratory) Route and rate II 7.1.1. and 7.2.1-7.2.3	Investigations are conducted under controlled laboratory conditions to evaluate both route and rate of degradation in soil for a period up to 120 day. **Guidelines:** Current EU guideline study is OECD307. However, older studies may have been conducted to SETAC 1995 (or US EPA) guidelines. OECD 307 – study conducted at 20°C and 40-60%MWHC. SETAC – study conducted at 20°C and 40-50%MWHC. EPA studies conducted at 25°C and 75% of 0.33bar soil moisture and are usually drier than the studies conducted according to OECD or SETAC. Criteria for US studies are different and are considered on a case by case basis.	➢ DegT50 (lab) of active substance under controlled temperature and soil moisture content. DegT50 should be normalised to 20°C and pF2 moisture content for use in FOCUS ground water assessment. ➢ Identity and formation percentage of metabolites and metabolic pathway. CO_2 mineralisation and bound residue formation. ➢ DegT50 (lab) of metabolites by kinetic modelling [FOCUS Kinetics]. ➢ Correlation of degradation rates with soil properties – pH, CEC, clay content, OM etc. ➢ Biphasic degradation can be indicative of kinetic sorption processes – degradation data can be analysed to derive Tier-1 kinetic sorption input parameters for ground water models (e.g. PEARL) [FOCUS Kinetics]. ➢ Aerobic degradation studies on sterile soils can indicate that abiotic degradation processes are important and allow default depth dependant degradation parameters to be adjusted. ➢ Degradation studies on subsoils can give useful information such as identifying that other degradation processes are important and allow default depth dependant degradation parameters to be adjusted.
Soil photolysis (Laboratory) Route and rate II 7.1.3	Investigations are conducted under controlled laboratory conditions to evaluate the effect of photolysis on both the route and rate of degradation. **Guidelines:** Current EU guideline study is SETAC 1995.	➢ Identifies if photolysis could be an important dissipation process (aqueous photolysis can also be an indicator). ➢ FOCUS models do not directly account for photolysis. If this is an important dissipation route then higher-tier parameterisation of the models is required for degradation.
Anaerobic soil degradation II 7.1.2 and 7.2.4-7.2.5	Degradation in soil is investigated under anaerobic (reducing) conditions. **Guidelines:** Current EU guideline study is SETAC 1995.	➢ Anaerobic soil studies can indicate that degradation will continue in anaerobic soil layers.

Study, Directive OECD Number	Description	Useful information
Field soil dissipation studies II 7.3	Degradation in soil under field conditions is investigated for up to 2 years. Typically four sites are investigated with a range of soil textures and climatic conditions representative of the intended use of the active substance. **Guidelines:** Current EU guideline is SETAC 1995	➢ DegT50 values are derived under more realistic use conditions for the active substance and metabolites. ➢ DegT50 values should be normalised to reference soil temperature and moisture content (20^{o}C and pF2) using daily measurements to derive more relevant values for use in risk assessments. ➢ Bulk soil movement of compounds can be evaluated. Typical soil units of 0-10, 10-20, 20-30 and 30-60cm are collected and analysed to show a residue free layer. Evaluation of the bulk soil profile with time (in combination with daily rainfall data) can show potential mobility of active substances and metabolites. ➢ DegT50 values can only be used as input parameters for modelling if transport processes such as leaching, runoff, and volatilisation are not important or can be quantified. Leaching is unimportant if the soil has been sampled to an adequate depth with a method of adequate sensitivity. A level field (sometimes with a soil berm around the plot) can minimize or eliminate runoff under most circumstances. Significant volatilisation losses are limited to a few compounds and often can be subtracted from the amount applied. Special care must be taken for compounds with two or more degradation mechanisms (such as soil photolysis and soil microbial degradation) so that the two different degradation mechanisms can be appropriately separated. ➢ Site-specific soil and weather data can be used to model the bulk soil movement. The simulation results can be compared to the measured field data in order to check if other processes are important such as aged-sorption. Such a comparison can also serve as a validation of these other processes for their use in ground water evaluations.

Study, Directive OECD Number	Description	Useful information
Adsorption desorption studies II 7.4.1-7.4.2	Sorption to soil is investigated under laboratory conditions according to OECD 106. **Guidelines:** Current EU guideline study is OECD106.	➤ The adsorption coefficients K_d, K_f, K_{oc} or K_{om} are determined for a range of soils. In addition, the Freundlich parameter (1/n) is also derived from studies conducted at multiple concentrations. ➤ Dependence of sorption on soil properties (pH, clay content, CEC, iron ferro-oxides etc) can be investigated. ➤ Sorption studies on subsoils can be useful for the evaluation of field studies. ➤ Desorption hysteresis can show if kinetic (aged) sorption with time is important. ➤ Streck kinetic sorption parameters for use in tier-1 ground water evaluations can be derived from the analysis of batch equilibrium adsorption desorption studies conducted according to OECD106.
Aged desorption studies	Increased sorption with time is determined from desorption experiments. The test compound is applied to soil and incubated under aerobic conditions (as per aerobic soil degradation study OECD 307). At various time points the soil sample is partitioned with $CaCl_2$ (as per batch equilibrium adsorption desorption study OECD 106) to allow K_d or K_f values to be derived. **Guidelines:** No test guideline currently exists, but the soil incubation is conducted according to OECD 307 and the batch equilibrium according to OECD 106.	➤ Kinetic sorption and degradation parameters can be derived from the evaluation of the data and used directly in higher-tier ground water evaluations. ➤ The increase in K_d with time throughout the study can be determined. ➤ Kinetic sorption data determined for soils collected from field dissipation studies can be used to validate higher-tier ground water evaluations.
Octanol water partition coefficient II 2.8.1	The octanol water coefficient (Log K_{ow}, Log P) is determined under laboratory conditions. Shake flask or HPLC method (K_{oc}). **Guidelines:** Partition coefficient octanol/water: Shake flask method OECD 107 (adopted 27 July 1995); Partition coefficient octanol/water: HPLC method, OECD 117 (adopted 13 April 2004)	➤ Useful for estimating plant uptake and also adsorption for minor metabolites. ➤ K_{om} can be estimated from Log K_{ow} using a number of empirical routines.

Study, Directive OECD Number	Description	Useful information
Soil TLC II 7.4.6	Thin layer plates of soil are prepared and the test compound applied. The plates are then developed with $CaCl_2$ solution and the R_f of the test compound compared to reference materials of known K_{oc}. **Guidelines:**	➢ Idea of potential mobility in soil. ➢ Comparative K_{oc} estimates from evaluation against reference materials.
Column leaching II 7.4.3-7.4.4	The test compound is applied to the top of a 30cm column packed with sandy soil and irrigated with 200mm water in 24 hours. Analysis of radioactivity in leachate and soil segments. **Guidelines:** OECD 312	➢ Idea of potential mobility in soil. ➢ K_d/K_{oc} estimates can be derived from comparative tests with reference compounds. ➢ K_d/K_{oc} estimates can be derived from evaluation of the soil segments using empirical formulae.
Column leaching (intact cores)	The test compound is applied to undisturbed soil columns and irrigated under controlled temperature water flow boundary conditions. High resolution analysis of the leachate is conducted with time. **Guidelines:** currently no guideline	➢ Analysis of the breakthrough curves of the tracer, test compound and metabolites allows detailed information on the sorption behaviour to be determined. ➢ K_{oc} and DegT50 values may be derived by inverse modelling.
Aged residue column leaching II 7.4.8	The test compound is applied to soil and incubated under aerobic conditions for one half-life. The soil sample is then added to the top of a 30cm column packed with sandy soil and irrigated with 200mm water in 24 hours. Analysis of radioactivity in leachate and soil segments. **Guidelines:** OECD 312	➢ Idea of potential mobility of major (and minor) metabolites in soil. ➢ K_d/K_{oc} estimates can be derived from comparative tests with reference compounds. ➢ K_d/K_{oc} estimates can be derived from evaluation of the soil segments using empirical formulae. (Fryer et al., 1996)[15]

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[15] Freijer, J.I., A. Tiktak, S.M. Hassanizadeh and A.M.A. van der Linden. 1996. Pestrasv3.1: A one dimensional model for assessing leaching, accumulation and volatilization of pesticides in soil. RIVM report no. 715501007, Bilthoven, The Netherlands.

Study, Directive OECD Number	Description	Useful information
Lysimeter studies II 7.4.7	Soil usually with a coarse (sandy) texture Rather high rainfall, supplemented by irrigation if not high enough For example BBA requirements often followed : % OC < 1.5 % rainfall (+ irrigation) >800 mm Maximum application rate and maximum number of applications expected, application timing at the period where leaching is expected to be maximised, but in line with the recommended GAP. Crop in agreement with the intended use or bare soil (considered as less favourable due to lower evapotranspiration) Study duration : often two lysimeters, one with single or multiple applications the first year and two-year leachate sampling, the other with single or multiple applications the first two years and three-year leachate sampling Radiolabelled material usually used **Guidelines:** BBA IV, 4-3 and Modification of the lysimeter guideline (Nachrichtenbl. Dt. PflSchD. 43, 1991). Guidance Document: OECD Series on Testing and Assessment, No. 22.	➢ Active substance and metabolites contents in the leachate (possibility of detection of metabolites that were not identified in the soil metabolism) ➢ Active substance and metabolites contents in the soil profile at the end of the study ➢ May allow parameter refinement for modelling (only if detailed soil and weather data are available). **Limitations :** No information about intermediate depths before the end of the study Hydrological specificities of a closed device. Mass flow of leaching compounds, however, measured to be higher compared to field plots (Jene et al., 1998). Agroclimatic and soil conditions typical of a small percentage of arable land in several countries, even if they are considered to be a worst-case for a variety of conditions (mostly close to FOCUS Hamburg scenarios)

Study, Directive OECD Number	Description	Useful information
Field leaching studies II 7.4.8 a) suction cups	Information about field soil hydrology (tensiometers…) Suction cups for water sampling (by application of a negative pressure) in the unsaturated and/or saturated zone or wells screened into the shallow ground water table. The material of the suction cups or wells must minimise adsorption. The installation of the suction cups must ensure a good contact between soil and cups (silica flour can be used to aid the hydraulic contact) and it is essential to prevent preferential flow along the tubes (bentonite is typically used to seal to within about 10cm of the suction cup). The cups and their pipes should not be installed in contaminated soil when measuring concentrations around 0.1 ppb because this is prone to give false postitives (better: installations from the side) It is also necessary to be careful of the possible effect of an artificial hydraulic gradient due to the pressure applied for sampling (samples should therefore only be collected when freely draining water is available i.e. when tensiometers show a positive pore water pressure / matrix potential). The depth of the water table must be specified.	➢ Concentrations in soil and water at different depths and different sampling dates in realistic field conditions ➢ Preferential flow can be investigated ➢ May allow parameter refinement for modelling (only if detailed soil and weather data are available). **Limitations :** No radiolabelling No balance for the active substance Concentration in water at different depths in the soil profile not necessarily reliable due to use of suction cups Spatial and temporal variations can make the interpretation of results rather complex

Study, Directive OECD Number	Description	Useful information
Field leaching studies II 7.4.8 b) ground water wells	Test fields are chosen that represent typical or worst case climatic, soil and ground water conditions for the use to be tested, depending on the objective of the study. The test field is extensively characterized with regard to soil and hydrological conditions. It should be large enough to be maintained with common agricultural equipment and practice. The field is equipped with a suitable number of ground water sampling wells, depending on the size of the field and the local ground water conditions. The wells must be in cluster (minimum 2 wells at 5 meters of distance) of at least three and will be placed in the field take into account the hydrology. The field is cropped with the target crop and is treated with the test substance according to the label. Samples of ground water are taken regularly (e.g. monthly) from the uppermost ground water and are analysed for the test substance or its derivatives. Additional sampling may include soil samples or water samples extracted from the unsaturated zone using e.g. suction cups. Additional data gathering that facilitates the interpretation of the results may include local weather data, soil moisture/water tension data, recording of the ground water level etc. The possibility to irrigate the field allows for additional options in the design of the study. The use of a conservative tracer may increase the acceptance of the study.	➢ Concentration in the target compartment (ground water = actual subject of protection) at different sampling dates under real practice conditions ➢ Total ground water load includes contribution of preferential flow ➢ Significant local point source entries (e.g. by preferential flow) are detectable by using a sufficient number of wells ➢ May allow for parameter refinement for modelling
Hydrolysis II 2.9.1 and II 7.5	The hydrolytic degradation of the test compound is studied under sterile conditions at various pH's (typical [4] 5, 7 and 9) **Guidelines:** OECD 111	➢ Can identify if abiotic hydrolytic degradation processes are significant for the test compound. ➢ If the test compound readily hydrolyses at environmentally relevant pHs then the default depth dependant degradation factors can be adjusted for a higher-tier evaluation. ➢ The effect of varying soil pH for each FOCUS scenario has to be considered.

Study, Directive OECD Number	Description	Useful information
Monitoring II 7.12	Information about quality of the wells, geology, aquifers (depth and characteristics like water infiltration rate), land use, list of compounds analysed, limit of detection and limit of quantification for each compound. It is possible to distinguish between general monitoring (for example national or regional programs of water quality control) and specific monitoring programs (in shallow or deeper aquifers) for one active substance and relevant metabolites decided by agrochemical companies and regulators.	➢ Comparison / validation of predicted concentrations ➢ Information on real concentrations in the aquifers and on long term tendencies ➢ Regional or local differences can provide information about more vulnerable areas, allowing for regional or local risk management. **Limitations :** Monitoring not possible before authorization of a substance, however post-registration monitoring programs possible Spatial and temporal variability difficult to interpret Aquifer recharge area not always well known Abstraction of water can modify the surrounding hydrology

APPENDIX 4: A METHOD TO DERIVE CROP-SPECIFIC LEACHING SCENARIOS

Introduction

The aim of the FOCUS ground water group was to develop a limited number of "realistic worst-case" leaching scenarios, which were broadly representative of agriculture in major agricultural production areas of the EU. In order to limit the number of simulation runs to a manageable size, the leaching scenarios are used to simulate pesticide applications to 25 crops, which were defined for each site according to the probability of occurrence in the respective agricultural region. For that reason FOCUS leaching scenarios represent a screening tool that reflect collectively realistic and vulnerable use conditions in relevant climate zones and agricultural areas in Europe. As a result of this regulatory framework, the following two characteristics of FOCUS scenarios should be considered:

1. FOCUS leaching scenarios were not designed to reflect the worst-case for the country from where weather files were obtained but reflect vulnerable situations that are representative for agricultural zones across various member states.

2. Each FOCUS scenario was parameterised with data for a range of crops. As a consequence the relative leaching vulnerability for a specific crop-location scenario varies with the crops for a given location. For major crops (e.g. cereals, maize) the scenario might reflect a realistic worst-case whereas for other crops the scenarios might be not representative at all (e.g. Hamburg/vines, Piacenza/citrus).

If simulations with FOCUS scenarios suggest that a more detailed analysis of leaching risk is required at the member state level, defining crop-specific worst-case scenarios on the basis of the actual cropping areas is appropriate. This appendix describes a method that can be used to identify candidate locations for new crop-specific scenarios. Specific guidance on the parameterisation of the new soil scenario files is given in Section 7.2.5. This section also recommends the context in which new cropping scenarios should be used within the FOCUS ground water framework for this purpose.

The proposed method intends to identify new, crop-specific leaching scenarios that can be calculated with the same FOCUS leaching models used in Tier-1. These higher tier scenarios are selected on the basis of the co-occurrence of climate, soil and crop properties, which are considered vulnerable for pesticide leaching. By overlaying the respective data layers in a GIS, the overall percentile of leaching vulnerability can be quantified in order to put the new scenarios in the context of the overall assessment of leaching risk. More realism

is thus introduced into the assessment since the overall percentile is specifically derived for the intended use area of a compound. The PECgw in Tier 2 is eventually calculated with a standard FOCUS leaching model which was parameterized with the new crop, climate and soil parameters and with country specific application data if appropriate. Except for the new scenario definition, the PECgw calculation follows the guidance for simulation runs in Tier-1.

The intention of this appendix is to provide guidance for harmonized higher-tier assessments at the EU and national level. For maximum harmonisation, the proposed method should be applicable to every member state in the EU. For that reason GIS data sets covering the entire EU are preferred (see fact sheets in Appendix 8). National soil data sets sometimes contain more detailed information and might be considered superior to European data for local assessments.

Identification of suitable indicators for leaching risk

Soil parameters

A number of soil properties influence the leaching behaviour of compounds, but due to limited availability of soil data restricting the vulnerability assessment to a few parameters is inevitable. The basic requirement is that the parameter should cause a pronounced sensitivity in leaching calculations with FOCUS models <u>AND</u> the spatial variation of this parameter should be available in the same resolution and quality for <u>ALL</u> member states in the EU.

Van den Berg et al. (2008) provide a sensitivity analysis for the GeoPearl model. Dubus et al (2000, 2003) conducted a sensitivity analysis for FOCUS leaching models and found that organic carbon content, bulk density and water content at field capacity are the most influential parameters in leaching calculations. The latter parameter is used in capacitance models for the simulation of soil water fluxes down the soil profile and is not present in models that solve the Richards equation. For that reason the sensitivity is dependent on the model. Bulk density is provided across the EU only in classified form, which prevents the use of this parameter in quantitative assessments. In view of these limitations the organic carbon content in topsoil was used as the primary indicator for leaching vulnerability. This decision was based on the following rationale:
- Calculated organic carbon contents are available as continuous data points (1 x 1 km) across the European Union (Jones et al. 2004, 2005).

- The organic carbon content is one of the most sensitive soil parameters in PRZM, PELMO, and PEARL. In this way the sensitivity is independent of the leaching model that is used in the assessment.

Special case: Interactions between soil and pesticide parameters

In cases where compounds degrade mainly via abiotic processes, the soil pH can also be an important indicator for site-specific degradation rates. Soil pH should be used as an additional indicator for leaching risk if pH-dependence of leaching risk is expected. In case of a clear relationship between soil pH and degradation rates the soil pH can be used as an additional indicator. The impact of soil pH on the sorption behaviour is sometimes of binary nature, which means that sorption changes abruptly once a specific pH level is passed. Such phenomena need to be considered on a case-by-case basis if appropriate.

Currently there is no reliable coverage of pH values in European soils. The best approximation of pH is provided by Batjes et al. (1995) who assigned average pH values to soil units based on the FAO names. The respective estimates for pH can be visualized by means of the EU soil map.

If the K_f of an active ingredient does not correlate with the organic carbon content in soils alternative indicators or multiple correlations with soil properties should be used. Beside pH such indicators could be textural parameters like clay content. As a general rule, the choice of spatial indicators should be based on existing knowledge about the factors that determine the mobility of the test substance. Sufficient evidence that a factor is exerting a significant influence on the mobility is either a high correlation of K_f or DegT50 with a specific soil parameter or, in exceptional cases, a more complex sensitivity analysis.

Climate parameters

In contrast to chemical leaching, Dubus et al. (2003) found that modelled percolation volumes were only slightly affected by variations of soil parameters, suggesting that meteorological variables will be the main drivers of water balance predictions. Therefore, for the majority of compounds the average sum of precipitation during the period of ground water recharge (October – March) and the mean annual temperature are the primary climate indicators for leaching vulnerability.

As a refinement of the original definition of FOCUS only rainfall volumes between October and March are considered if the compound is likely to be present in soil at the onset of the recharge period. This approach is based on the following rationale:

- Ground water recharge is most likely occurring outside the vegetation period when evapotranspiration is low and soil moisture is close to saturation. Northern European soils are typically saturated after autumn rainfalls and again at the end of winter during snowmelt. A similar cycle can be observed in southern Europe although the absolute volume of ground water recharge is smaller.
- From spring until late summer the overall water balance is likely to be negative for most agricultural areas in Europe. A rough calculation of water excess in the MARS data base (= precipitation minus evapotranspiration) during April and September reveals that only in small regions the water balance is positive in summer (see Chapter 13).

A further advantage of this pragmatic approach is that uncertainties with regards to irrigation practices during the vegetation period are minimized.

The current resolution of the European climate database MARS is 50 x 50 km, which is a rather coarse resolution when performing the analysis for small cropping areas. In cases where higher-resolution climate data are available, the resulting smaller grid-size would be preferable because it is closer to the scale of the soil information.

Temperature is an important discriminator as this parameter influences both the calculated volumes of leachate as well as the degradation of chemicals.

Special Case: Interactions between climate and pesticide parameters

Van der Linden et al. (2004) suggest that the leaching behaviour of compounds with a DegT50 of less than 10 d and a K_{om} below 10 L kg^{-1} (K_{oc} of 17 L kg^{-1}) is highly influenced by seasonal climate patterns. In the case of short-lived compounds with very low sorption capacity in soils, the 3-month period after application is most appropriate. If the same compound is applied in autumn, winter rainfall should be used.

Rainfall volumes and temperatures within the cropping area can be extracted from the MARS (2004) weather data base, which contains daily weather data from 1992 – 2003 in 50 x 50 km

grid cells. MARS was also the source of FOCUS climate files and is therefore the most appropriate data base to perform an analysis of spatial leaching risk in a Tier-II assessment.

Identifying locations for crop-specific worst-case scenarios

The area of interest

In a first step, the cropping area is identified to ensure that calculated leaching vulnerabilities reflect only the cropping area. Some perennial crops like olives or vineyards are included as separate classes in Corine Land Cover (Corine, 2000) and thus their regional occurrence can be visualised with a high spatial accuracy. Individual fruit and field crops have to be visualised by means of agricultural census data since Corine Land Cover does not differentiate between crops on arable land or orchards.

In order to give a practical example of the application of the method, a virtual use in French sugar beets was chosen in this section. In France the best source of statistical data is the agricultural census of 200 at the level of *cantons* (Nuts 4), which is available through the National Office of Statistics (SCEES, 2000). The area of interest was subsequently defined as "any canton where sugar beets are grown on at least 100 ha". The threshold of 100 ha was chosen in this particular example because it is likely areas < 100 ha are not shown in Nuts-4 data because of data protection regulations. If Nuts-3 data are used (i.e. *Départments* in France) a higher threshold value is appropriate and needs to be justified based on the simulated crop.
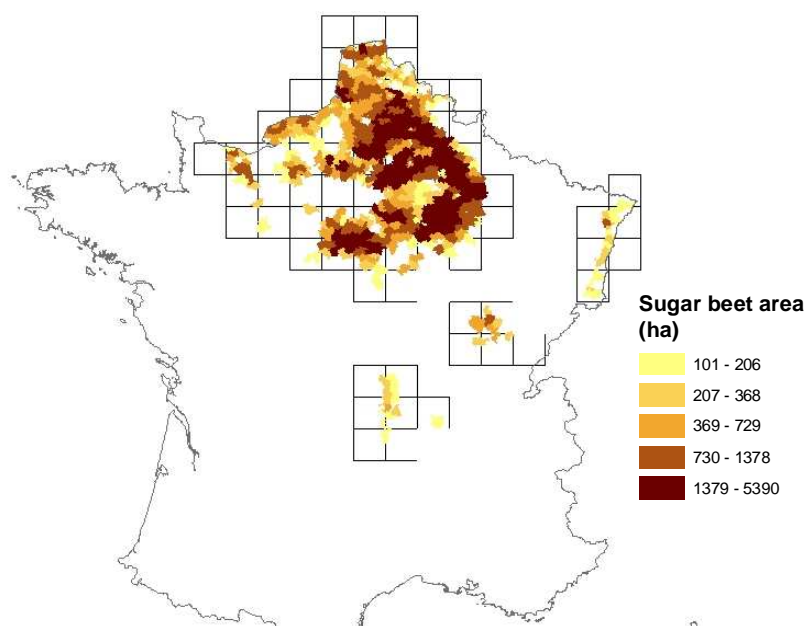
Figure A4-1. Cropping area for sugar beets in France (canton-level) and pertinent MARS climate cells (Sources: SCEES, 2000; MARS, 2004).

Assessing the joint vulnerability of climate and organic carbon contents

To assess the relative vulnerability of a grid cell, its relative ranking with regards to climatic conditions in the entire cropping area of a specified crop must be known. Temperature, rainfall and organic carbon contents can be expressed as the percentile values of a normal distribution function. By adding three normal distribution functions, the joint percentile value can be calculated and thus the joint vulnerability of the location.

Unit of analysis

The available datasets on climate and soil properties show different spatial resolutions and raster sizes. For that reason a suitable unit at which all parameters can be aggregated must be defined. For the purpose of this assessment, the MARS grid (50 x 50 km) was chosen as the unit of the analysis.
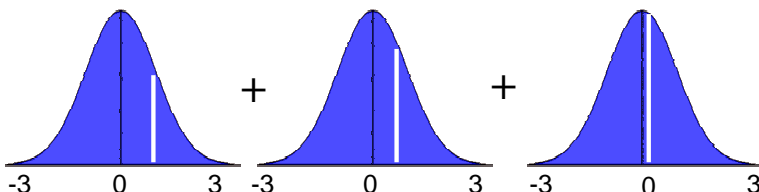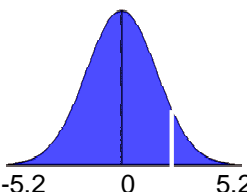
Calculation percentiles of vulnerability

Assuming that all variables are normally distributed and have a similar effect on leaching, three normal distributions with a mean of zero and standard deviation of 1 can be added to calculate the joint percentile of vulnerability. The joint distribution percentile is the value (p_rainfall + p_temperature + p_organic carbon) on the joint normal distribution with a standard deviation of $\sqrt{3}$. Table A4-1 illustrates the approach by means of a numerical example.

Table A4-1. Example for the calculation of joint percentiles for rainfall and temperature.

Single probabilities						Joint probability	
1	2	3	3	4	5	6	7
	Single percentile		Corresponding values in the normal distribution function with mean of 0 and **stdev of 1**			col. $3+4+5$	Percentile of col. 6 in the joint normal distribution with mean of 0 and **stdev of √3**
Winter rainfall	Tem-perature	Organic carbon	Rain-fall	Tem-perature	OC		
89th	84th	51st	1.23	0.99	0.003	2.25	**90.3rd**

-3 0 3	-3 0 3	-3 0 3	-5.2 0 5.2
89th percentile = 1.23 in distribution N(0,1)	84th percentile = 0.99 in distribution N(0,1)	51st percentile = 0.003 in distribution N(0,1)	90th percentile = 2.25 in distribution N(0,√3)

In order to avoid extreme values introducing bias into the assessment, all raster cells at an altitude greater than 700 m were excluded. The altitude of 700 m was chosen for pragmatic reasons, since it is the minimum altitude that qualifies farms for participation in EU programs for support of farms in mountainous regions.

Figure A4-2 and Figure A4-3 show mean annual temperatures and average amounts of winter rainfall from 1992 – 2002 for the cropping area of sugar beets in France. In the next step organic carbon contents are added to the unit area of analysis.
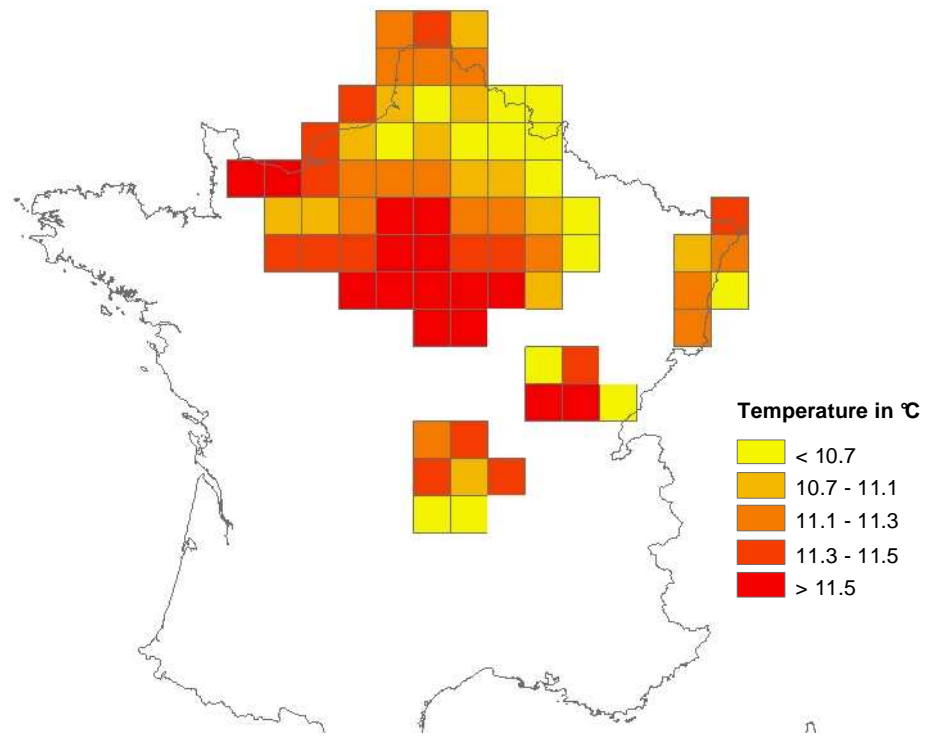
Figure A4-2. Annual average temperatures (Source: MARS, 2004).
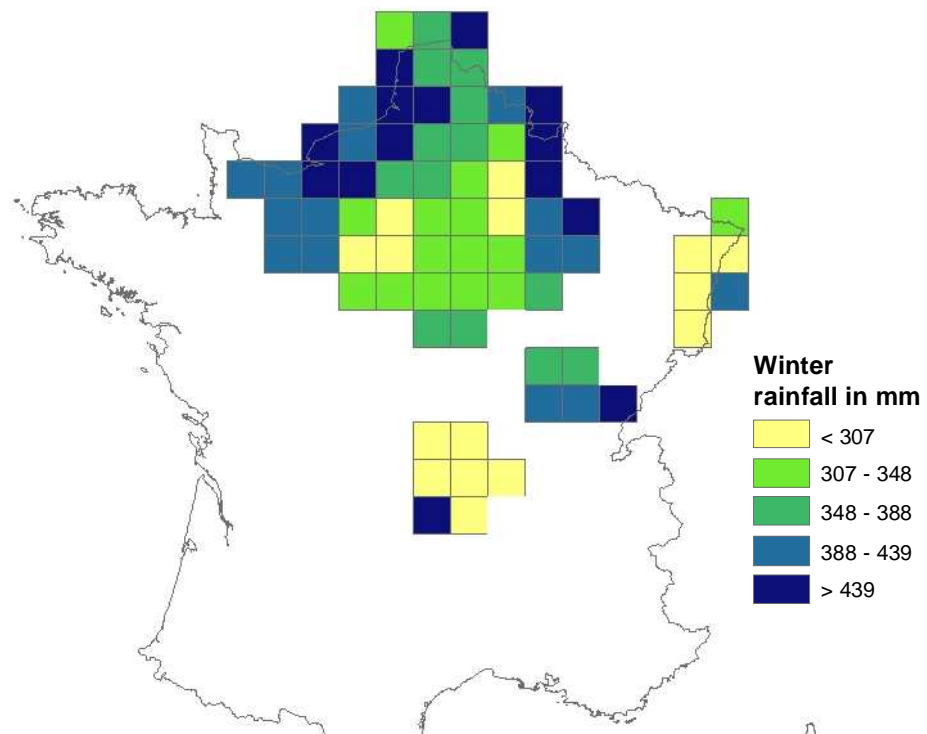
Figure A4-3. Average winter rainfall (Source: MARS, 2004).

The map of organic carbon contents of European topsoils (Jones et al. 2004, 2005) gives organic carbon contents for all land use classes. For that reason, the analysis must be restricted to arable land before deriving an overall mean organic carbon content per unit area. The most appropriate data base for identifying arable land is Corine Land Cover (Corine, 2000). A simple overlay of these datasets yield organic carbon contents in topsoils of arable land within the area of interest (Figure A4-4). The mean organic carbon content is subsequently calculated for the unit of analysis and used for the final calculation of vulnerabilities (Figure A4-5).
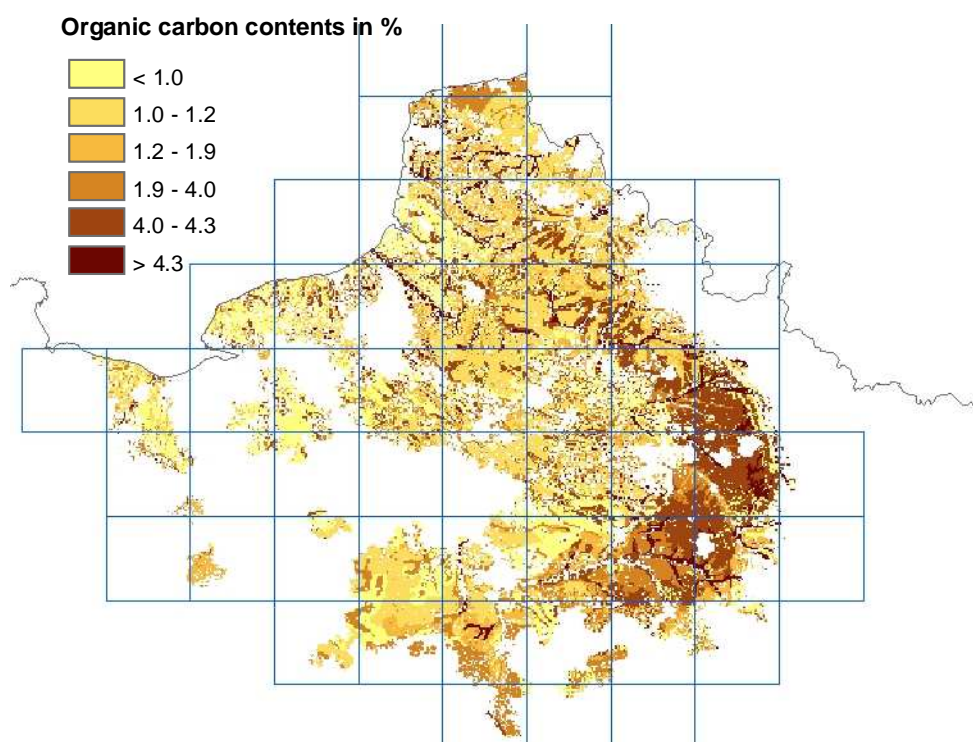
Figure A4-4. Organic carbon contents for arable land in the main sugar beet area (Sources: Jones et al., 2004; 2005).
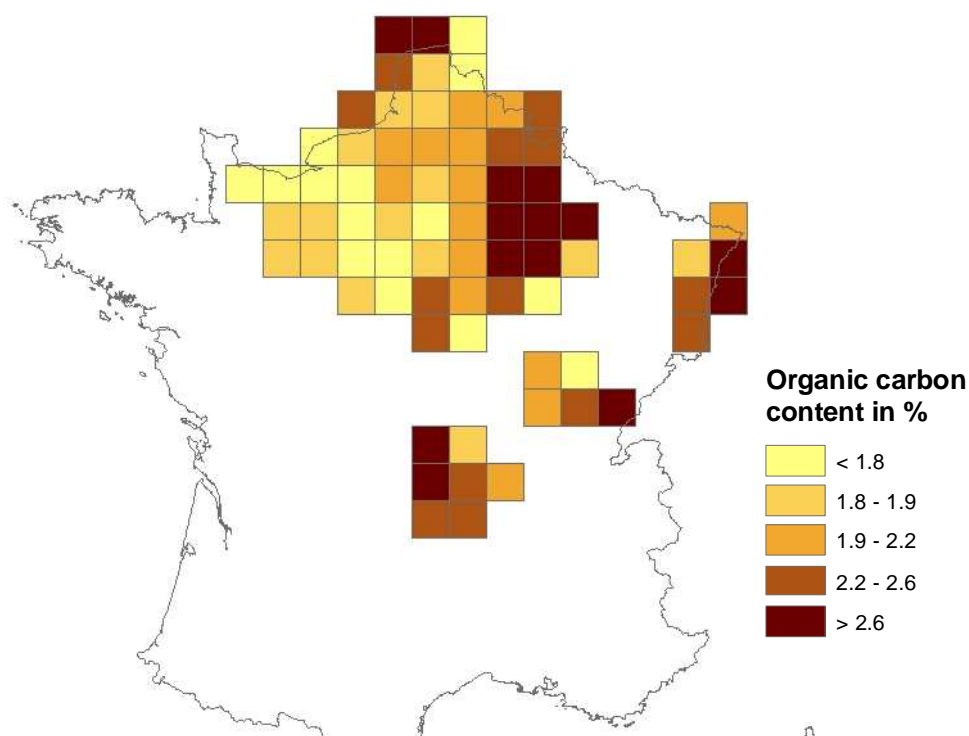
Figure A4-5. Organic carbon contents for arable land aggregated for the unit of analysis (Sources: Jones et al., 2004; 2005).

The calculated percentile values for winter rainfall, temperature and organic carbon contents are subsequently summarized for each unit area and converted into a joint percentile value on the joint normal distribution. If the assumption of an equal contribution of each factor is accepted then all factors can just be added to give rise to a joint vulnerability index. In many cases the contribution of rainfall, temperature or organic carbon contents is however not equal. For that reason a sensitivity analysis should be performed to find reasonable estimates for weighting factors. The respective procedure is described in the following section.

Compound-specific weighting factors

Method

In the following section, the specific contribution of e.g. rainfall or content of organic carbon to the leaching risk is assumed to differ with compound properties. As a result, this approach may result in different scenarios for two compounds with the same use pattern (crop, application date etc).

The sensitivity analysis was performed with FOCUS PEARL 2.2.2 and the Piacenza and Châteaudun leaching scenarios with the goal to assign weighting factors to the main

310

parameters in the vulnerability index. Note that this analysis can be extended if other parameters (such as pH or texture) have a significant influence on the leaching risk of a compound. The current example focuses on rainfall, temperature and organic matter contents in soil and is used to illustrate the approach.

The sensitivity analysis was done with four example compounds. The respective properties are summarized in Table A4-2. All compounds are "dummy compounds," which were defined by previous FOCUS working groups to test the performance of models. Dummy A – C were defined by FOCUS (2000) for ground water and Dummy 3 by FOCUS (2002) for surface water. All compounds were assumed to be herbicides that are applied one day before emergence of winter wheat.

Table A4-2. Compound properties used in the sensitivity analysis

Parameter	Unit	Dummy A	Dummy B	Dummy D	Dummy 3
Mol. mass	g/mole	300	300	300	221
Vapour pressure	Pa	$1.0 E^{-7}$	$1.0 E^{-7}$	$1.0 E^{-7}$	$1.0 E^{-5}$
Sol. in water	mg/L	90	90	90	620
DegT50 soil	d	60	20	20	4
K_{om}	L/kg	60	10	35	0.58
K_{oc}	L/kg	103	17	60	1
1/n	(-)	0.9	0.9	0.9	1.0
Crop		Winter cereals	Winter cereals	Winter cereals	Winter cereals
Application rate	kg/ha	1.0	1.0	1.0	1.0

The simplest form of sensitivity analysis, one-at-a-time analysis, was used in this section. Each input parameter is varied independently one at a time with all other parameters being constant. The same approach was used to assess the sensitivity of FOCUS leaching models by Dubus et al. (2003).

The assessment of model sensitivity is based on the relative variation in model output (i.e. PECgw) for individual input parameters to the sum of variation of model output. The relative variation is thus calculated as follows:

$$RV_i = \frac{abs(PEC\max - PEC\min)}{PEC_{BC}}$$ (A4-1)

where:

RV$_i$ = ratio of variation for the landscape parameter i

PECmax = maximum PEC in sensitivity analysis for the landscape parameter i

PECmin = minimum PEC in sensitivity analysis for the landscape parameter i

PEC$_{BC}$ = PEC value in base case scenario

The weighting factor for landscape parameter i is subsequently calculated by dividing the ratio of variation of the single factor by the sum of the variation of all landscape factors:

$$f_i = \frac{RV_i}{\sum RV_i} \qquad \text{(A4-2)}$$

Example sensitivity analysis

The Piacenza and Châteaudun winter cereals scenario in FOCUS PEARL 2.2.2 were used as the base case in this study to ensure that the selection of a particular FOCUS Tier 1 scenario does not impact the results.

Selection of upper and lower boundaries for the sensitivity analysis. Depending on the landscape one parameter may show a larger variation than another. For that reason, the regional variation of rainfall, temperature and organic carbon should be analyzed first. The simplest indicator for the comparison of the variability of landscape factors is the coefficient of variation. In the sugar beet area in France organic carbon contents vary most, followed by winter rainfall and temperature.
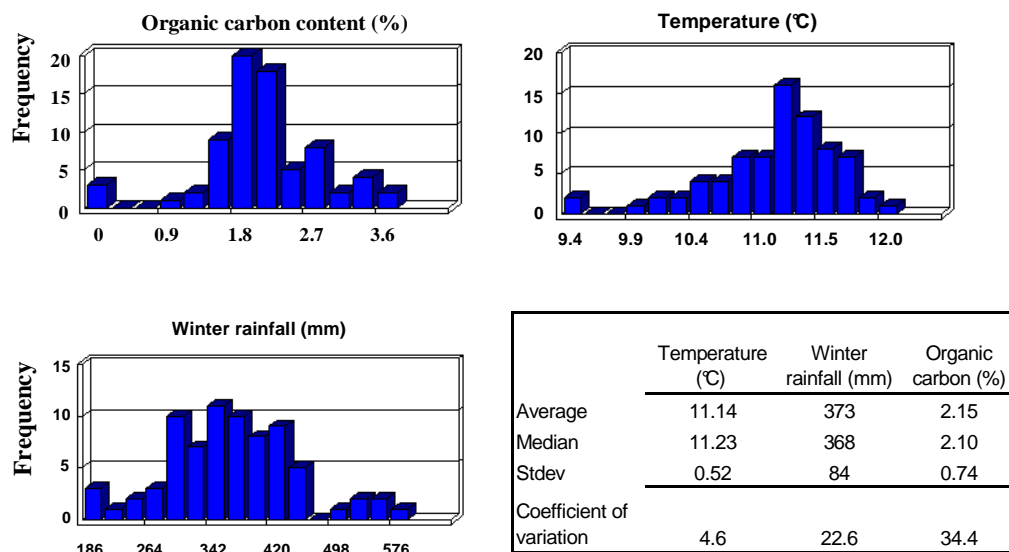
Figure A4-6. Spatial variation of landscape factors in the test area.

	Temperature (°C)	Winter rainfall (mm)	Organic carbon (%)
Average	11.14	373	2.15
Median	11.23	368	2.10
Stdev	0.52	84	0.74
Coefficient of variation	4.6	22.6	34.4

The coefficient of variation was used to determine the upper and lower boundary for the sensitivity analysis. This means temperature was varied by +/- 4.6% around the mean temperature of the Piacenza and Châteaudun scenarios, winter rainfall was varied by +/- 22.6%, organic carbon contents were varied by +/- 34.4%. The resulting PECgw is shown in Table A4-3. The modifications where implemented in FOCUS PEARL 2.2.2 *.met files by multiplying rainfall and min/max temperatures with the respective factors. The modified organic matter content was assigned to the first soil building block (PIAC-SU1; CHAT-SU1).

Table A4-3. Calculated combinations of factors and resulting PECgw.

	Winter Rainfall (mm)	Annual avg. Temperature (°C)	OM (%)	PECgw			
				Dummy A	Dummy B	Dummy D	Dummy 3
Base case Piacenza	**437**	**13.2**	**1.72**	**11.48**	**23.25**	**1.69**	**3.12**
plus 22.6 % rain	536	13.2	1.72	15.30	32.79	4.83	6.38
minus 22.6 % rain	338	13.2	1.72	5.14	7.51	0.60	1.13
plus 4.6 % temp	437	13.8	1.72	10.24	22.29	1.43	2.86
minus 4.6 % temp	437	12.6	1.72	12.90	24.32	1.99	3.39
plus 34.4 % OC	437	13.2	2.31	6.01	19.22	0.83	3.04
minus 34.4 % OC	437	13.2	1.13	19.70	28.00	4.04	3.20
Base case Châteaudun	**331**	**11.3**	**2.4**	**2.45**	**8.72**	**0.16**	**3.12**
plus 22.6 % rain	406	11.3	2.4	5.63	21.06	0.73	6.38
minus 22.6 % rain	256	11.3	2.4	0.33	2.34	0.00	1.13
plus 4.6 % temp	331	11.8	2.4	2.01	7.94	0.12	2.86
minus 4.6 % temp	331	10.7	2.4	2.96	9.59	0.21	3.39
plus 34.4 % OC	331	11.3	3.2	1.27	6.53	0.07	3.04
minus 34.4 % OC	331	11.3	1.6	5.30	12.02	0.43	3.20

Results. Table A4-4 summarizes the maximum ratios of variation and the resulting
weighting. The weighting factor expresses the relative contribution of each parameter to the
overall leaching risk.

**Table A4-4. Summary of maximum ratios of variation and resulting weighting factors for
rainfall, temperature and organic matter content in topsoil.**

	Dummy A		Dummy B		Dummy D		Dummy 3	
	Ratio of variation	weighting factor	Ratio of variation	weighting factor	Ratio of variation	weighting factor	Ratio of variation	weighting factor
Piacenza								
Rainfall +/- 22.6 %	0.89	**0.38**	1.09	**0.70**	2.50	**0.53**	1.68	**0.88**
Temp. +/- 4.6 %	0.23	**0.10**	0.09	**0.06**	0.33	**0.07**	0.17	**0.09**
OM +/- 34.4 %	1.19	**0.52**	0.38	**0.24**	1.90	**0.40**	0.05	**0.03**
Sum	2.31	1.00	1.55	1.00	4.73	1.00	1.90	1.00
Châteaudun								
Rainfall +/- 22.6 %	2.16	**0.52**	2.15	**0.72**	4.56	**0.62**	1.68	**0.88**
Temp. +/- 4.6 %	0.39	**0.09**	0.19	**0.06**	0.56	**0.08**	0.17	**0.09**
OM +/- 34.4 %	1.64	**0.39**	0.63	**0.21**	2.25	**0.31**	0.05	**0.03**
Sum	4.20	1.00	2.97	1.00	7.38	1.00	1.90	1.00

The proposed method allows for a quick assessment of the relative contribution of three environmental parameters that are assumed to influence the leaching behaviour of compounds. Due to its simplicity, the method can be applied routinely before deriving a vulnerability index by means of GIS methods. Note that the relative contribution of organic matter content, rainfall and temperature varies to a greater extent with decreasing sorption capacity. Dummy 3 has a K_{oc} of 1; therefore the content of organic carbon is almost irrelevant for the explanation of the leaching behaviour of the compound. In this case other parameters should be checked to determine whether they are a better descriptor to differentiate regional leaching vulnerability (e.g. pH or texture). If this is not the case then the assessment should be restricted to climate properties only.

The sensitivity analysis for four FOCUS dummy compounds revealed that the selected base-case has only a minimal effect on the resulting weighting factors. For the sake of practicality, the work group suggests to use only those FOCUS scenarios as base cases in which 0.1 µg/L were exceeded in Tier 1. The resulting weighting factors would then be the average factors found in these runs.

Figure A4-7 shows a comparison between the relative leaching risk of Dummy A and Dummy 3 for the sugar beet area using the average weighting factors. The compounds show different weighting factors and thus illustrate the impact of compound properties in the method..
The resulting overall vulnerabilities for Dummy A are shown in Figure A4-7.

Dummy A (OC = 0.45, rain = 0.45, temp = 0.10)   Dummy 3 (OC = 0.03, rain = 0.88, temp = 0.09)
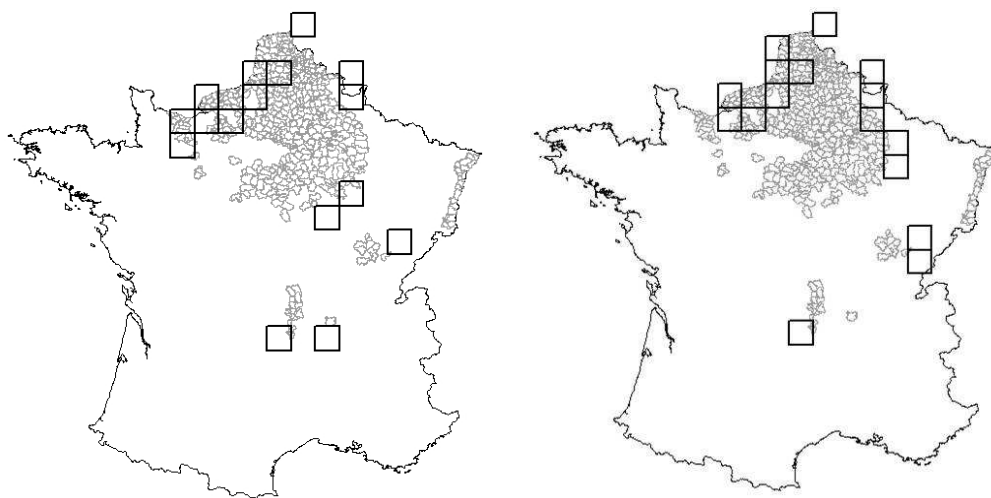
Figure A4-7. Raster cells that exceed the 80th percentile leaching risk for Dummy A and Dummy D.

Discussion of calculated leaching vulnerabilities

The present example shows that the variation of temperature is lower than the variation of rainfall or organic carbon contents. Variation of temperature is often small for crops, which are grown in confined agricultural regions or require a narrow range of annual average temperature for optimal growth. This phenomenon is reflected in the weighting factors. Note that in regions with a more pronounced variation of temperature (e.g. the cropping area for cereals) the weighting factor for temperature effects may be higher. Simulations with the final crop-specific scenario will be done with daily weather data from the respective climate grid cell. Therefore, the year-by-year variation of weather is considered in the simulations.

The individual contribution of soil and climate parameters to the overall leaching vulnerability is considered. Note that the proposed method is completely flexible if other parameters than OC, winter rainfall or annual average temperatures are considered important. A prominent example would be pH-dependent sorption or degradation. The new Dutch decision tree for the evaluation of pesticide leaching from soils states that the leaching behaviour of

compounds with a DegT50 < 10 d and a K_{om} < 10 L/kg would be more influenced by seasonal rainfall and temperature like the first 2-3 months after application.

Another assumption relates to the hypothesis of a normal distribution of winter rainfall, temperature and organic contents. Figure A4-6 shows the frequency distributions of all landscape factors. Even though the distributions did not follow exactly a normal distribution curve, a normal distribution was nevertheless considered to be the most practical solution for the ranking the leaching risk within grid cells.

Selection of candidate scenarios

General considerations

In accordance with the proposed vulnerability concept the target, vulnerability is the 90[th] percentile worst-case situation. In addition, a range of PECgw values should be provided to account for temporal variations of weather patterns that are not well captured when using mean values. For that reason the following four scenarios should be considered:

- The location closest to the overall 90[th] percentile of rainfall, temperature and organic carbon content
- The location that reflects the 90[th] percentile winter rainfall without exceeding the overall 90[th] percentile
- The location that reflects the 90[th] percentile annual average temperature without exceeding the overall 90[th] percentile
- The location that reflects the 90[th] percentile worst-case organic carbon content without exceeding the overall 90[th] percentile

PECgw (80[th] percentile) values below 0.1 µg/L at all locations would imply that the product is safe under realistic worst-case conditions in the cropping area for which the assessment was conducted.

The modeller must ensure that all scenarios reflect realistic conditions for the target crop when extracting the required scenario data from MARS and the EU soil map.

Selection of scenario areas (grid cells)

The area of a climate scenario is confined by the MARS 50 x 50 km grid cells. The proposed percentile approach allows for a ranking of these grid cells in order to identify appropriate candidate scenario areas. In the case of small cropping areas it is likely that the 90[th] percentile is not present as such but a 89[th] or 91[st] percentile. It is also likely that certain grid cells are present in the sample of grid cells although their share in the total cropping area of the target crop is only marginal. In the following example, the selection of suitable grid cells is described on the basis of the sugar beet example in France.

In a first step all grid cells are selected that fall between the 85[th] and 95[th] percentile range. This query is repeated for the four target vulnerabilities described above, *i.e.* 90[th] percentile of all parameters, 90[th] percentile for rainfall, temperature and OC.

Table A4-5. Summary of grid cells that fall between the 85[th] and 95[th] percentile for total vulnerability.

Grid Cell	Avg. Temp. (°C)	Avg. winter rainfall (mm)	Mean OC (%)	Percentiles (Substance A)			
				OC	Winter rain	Temp.	Total
52051	10.8	380	1.7	83.8	56.7	78.4	79.7
54044	**11.0**	**432**	**1.9**	**69.0**	**77.0**	**70.3**	**81**
46048	10.2	531	2.5	23.0	95.9	96.0	82.4
56047	10.7	463	2.1	48.7	89.1	83.8	83.7
57047	10.9	442	1.9	67.6	82.4	71.7	85.1
55044	11.7	408	1.4	93.3	63.5	10.9	86.4
57051	10.6	551	2.4	28.4	97.2	87.9	87.8
56045	11.3	442	1.8	79.8	81.0	37.9	89.1
55045	**11.4**	**444**	**1.8**	**78.4**	**85.1**	**31.1**	**90.5**
57048	10.8	443	1.8	73.0	83.7	82.5	91.8

Grid cell 55045 is closest to the 90[th] percentile and is thus selected as a candidate scenario area. Grid cell 54044 reflects the 80[th] percentile and may be selected as an alternative scenario to represent the lower boundary of the 85 – 95[th] percentile range.

The selection procedure is repeated for all other target percentiles accordingly.

Table A4-6. Summary of grid cells that fall between the 85th and 95th percentile for <u>temperature</u> vulnerability

Grid Cell	Avg. Temp. (°C)	Avg. winter rainfall (mm)	Mean OC (%)	Percentiles (Substance A)			
				OC	Winter rain	Temperature	Total
59049	11	461	1.0	96.0	87.8	79.8	95.9
57050	11	417	2.0	54.1	68.9	81.1	68.9
57048	11	443	1.8	73.0	83.7	82.5	91.8
56047	11	463	2.1	48.7	89.1	83.8	83.7
56049	11	350	2.1	51.4	40.5	85.2	51.3
50051	11	361	2.3	37.9	44.5	86.5	44.5
57051	11	551	2.4	28.4	97.2	87.9	87.8
53052	11	440	2.0	58.2	79.7	89.2	78.3
52056	11	390	3.9	0.0	60.8	90.6	4.0
54052	**10**	**515**	**2.8**	**12.2**	**93.2**	**91.9**	**64.8**
55051	**10**	**531**	**3.5**	**4.1**	**94.5**	**93.3**	**52.7**

Grid cell 54052 is closest to the 90th percentile for temperature. However this cell is located just at the edge of the cropping area and is most likely not a suitable scenario area. In this case the next worse grid cell may be selected (55051).

Table A4-7. Summary of grid cells that fall between the 85th and 95th percentile for <u>rainfall</u> vulnerability.

Grid Cell	Avg. Temp. (°C)	Avg. winter rainfall (mm)	Mean OC (%)	Percentiles (Substance A)			
				OC	Winter rain	Temperature	Total
53052	11	440	2.0	58.2	79.7	89.2	78.3
56045	11	442	1.8	79.8	81.0	37.9	89.1
57047	11	442	1.9	67.6	82.4	71.7	85.1
57048	11	443	1.8	73.0	83.7	82.5	91.8
55045	11	444	1.8	78.4	85.1	31.1	90.5
49053	9	456	3.4	5.5	86.4	98.7	47.2
59049	11	461	1.0	96.0	87.8	79.8	95.9
55046	11	463	1.6	86.5	89.1	55.5	94.5
56047	11	463	2.1	48.7	89.1	83.8	83.7
58047	**11**	**468**	**2.5**	**24.4**	**91.8**	**46.0**	**66.2**
54052	10	515	2.8	12.2	93.2	91.9	64.8
55051	10	531	3.5	4.1	94.5	93.3	52.7

Cell 56047 may be chosen to represent the realistic worst-case rainfall scenario.

Table A4-8. Summary of grid cells that fall between the 85[th] and 95[th] percentile for <u>organic I</u>

Grid Cell	Avg. Temp. (°C)	Avg. winter rainfall (mm)	Mean OC (%)	Percentiles (Substance A)			
				OC	Winter rain	Temperature	Total
55045	11	444	1.8	78.4	85.1	31.1	90.5
56045	11	442	1.8	79.8	81.0	37.9	89.1
51049	12	368	1.7	81.1	50.0	1.4	58.1
58049	11	367	1.7	82.5	48.6	43.3	71.6
52051	11	380	1.7	83.8	56.7	78.4	79.7
55043	12	408	1.7	85.2	63.5	17.6	77
55046	11	463	1.6	86.5	89.1	55.5	94.5
54048	12	338	1.6	87.9	31.0	0.0	41.8
53047	12	297	1.6	89.2	12.1	13.6	45.9
54046	**11**	**315**	**1.6**	**90.6**	**24.3**	**50.0**	**63.5**
52047	12	322	1.5	91.9	28.3	8.2	60.8
55044	12	408	1.4	93.3	63.5	10.9	86.4

Cell no. 54046 is closest to the 90[th] percentile organic carbon content and was therefore chosen as the scenario area.

Summary of workflow

<u>Step 1</u>: Run FOCUS Tier 1 scenarios for the proposed use pattern. If PECgw is > 0.1 µg/L in scenarios that are deemed relevant for the intended area of use go to Step 2.

<u>Step 2</u>: Identify the area of interest on the basis of agricultural census data with an appropriate spatial resolution.

<u>Step 3</u>: Identify key landscape parameters that govern the leaching risk of a compound (e.g. OC, pH, texture, climate) and perform a spatial overlay of these datasets. Climate data should be taken from the EU MARS data base, soil properties are provided by the EU soil map or any national soil dataset that is considered superior to EU data. Organic carbon contents are provided as a raster map with 1 km resolution. For further information on publicly available GIS layers on the EU level consult Appendix 8.

Step 4: Analyse the coefficient of variation of these key landscape parameters within the area of interest and perform a sensitivity analysis with a FOCUS leaching model and the relevant Tier 1 scenarios in which 0.1 ppb were exceeded. The result of the sensitivity analysis is a weighting factor for each landscape parameter.

Step 5: Perform a spatial join of attribute tables and export to Excel. Table A4-9 gives an indication of the required fields that were used in the present example for French sugar beets.

Table A4-9. Fields required in the example for French sugar beets.

MARS ID	Temperature	Winter rainfall	Organic carbon (%)	Percent rank			Single probabilities			Joint probabilities	
	(°C)	(mm)	mean	Organic carbon	winter rainfall	temp	OC	rain	temp	weighting	Final percentile
1	2	3	4	5	6	7	8	9	10	11	12

1. ID number of MARS 50 x 50 km grid cell.
2. Annual average temperature given in grid cell.
3. Annual average winter rainfall given in grid cell.
4. Organic carbon from 1 km raster map averaged for MARS grid cell.
5. =IF(1-PERCENTRANK(array_[4];[4]) = 0; 0.00001; IF(1-PERCENTRANK array_[4];[4]) = 1; 0.9999; 1-PERCENTRANK(array_[4];[4])))
   The IF statement is required because the values of 1 and 0 cannot be interpreted otherwise.
6. =IF(PERCENTRANK(array_[3];[3]) = 0; 0.00001; IF(PERCENTRANK array_[3];[3]) = 1; 0.9999; PERCENTRANK (array_[3];[3])))

7. IF(1-PERCENTRANK(array_[2];[2]) = 0; 0.00001; IF(1-PERCENTRANK array_[2];[2]) = 1; 0.9999; 1-PERCENTRANK (array_[2];[2])).
8. =NORMINV([5];0;1) [position on Normal Distribution with a mean of 0 and a standard deviation of 1].
9. =NORMINV([6];0;1).
10. =NORMINV([7];0;1)
11. =([8] * factor) + ([9] * factor) + ([10] * factor)
    If all factors are of equal importance the weighting factor equals 1, otherwise the

weighting factors are calculated in the present example as

factor = 3 * weighting factor from sensitivity analysis

12. NORMDIST([11];0;(SQRT(3));1)

Joint distribution with a mean of 0 and a standard deviation of √3.

Step 6: Join Excel calculations in GIS with attribute table of MARS grid cells and identify cells close to the target percentile for vulnerability.

Step 7: Identify appropriate soil units within the selected grid cells. Soil profile data are extracted from SPADE data base of EU soil map. Average organic carbon contents in topsoil for the MARS grid are taken from the 1 km raster map. Daily weather data are extracted from MARS grid data base.

Step 8: If appropriate add irrigation volumes to weather file.

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APPENDIX 5. A TIERED APPROACH TO SPATIALLY DISTRIBUTED MODELLING

A. Tiktak

A5.1 Introduction

Spatially-distributed leaching models provide the user with maps of the predicted leaching concentrations in the intended use area or in a climatic zone. Frequency distributions and percentiles of the leaching concentration can be directly inferred from these maps (Figure A5-1). Spatially distributed leaching models are therefore important tools in the identification of tier I scenarios (Chapter 11), identification of use-specific scenarios (Section 7.2) and in higher tier national risk assessments (Section 8.2).
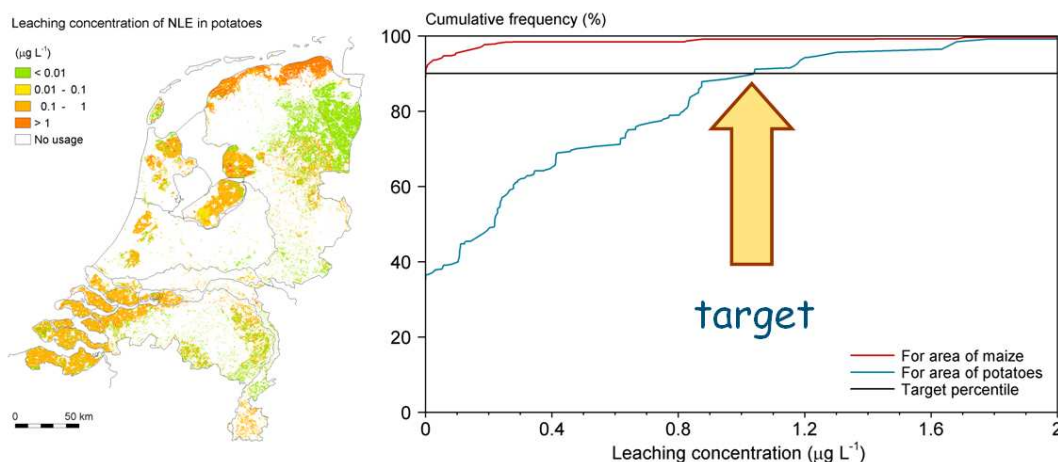
Figure A5-1. Percentiles of the leaching concentration in the intended use area can be inferred from the frequency distribution of a leaching map. Example with substance "NLD" in potatoes (conform Tiktak et al., 2003).

Spatial patterns of pesticide leaching can be directly simulated with process-based models, for example one of the FOCUS leaching models. Most approaches to spatially-distributed, process based numerical modelling come down to running a leaching model for several (often more than 1000) scenarios and putting the results in a map. This kind of process based numerical leaching models can be parameterised for the catchment scale (Petach et al., 1991; Leterme et al., 2004, 2006), the regional scale (Capri et al., 2000), the national scale (Tiktak et al., 1996; 2002a) and the European scale (Tiktak et al., 2004). The scenarios are usually constructed by spatially overlaying basic maps in a Geographical Information System. With respect to pesticide leaching, maps of soil-types, climate-classes,

crop-types and ground water-depth-classes are of particular interest. The disadvantage of process based spatially distributed models is that they contain a large number of parameters, which may be difficult to identify directly or which may not be available at larger scales.

To mitigate the above mentioned problems, simpler leaching models could be used to assess the leaching pattern. Many authors have used process-based, analytical or impulse response models for this purpose. The best known models of this type are the attenuation factor (Loague et al., 1989; 1996, Loague and Corwin, 1996) and the transfer function (Jury and Roth, 1990; Stewart and Loague, 2003; 2004). Analytical models do not account for vertical heterogeneity and assume steady-state conditions, so that they may not be compatible with results from numerical models. An alternative to the direct use of simpler models and a way to maintain the dominant behaviour of the more complex process-based model is to reduce the complex leaching model into the mathematical form of the simple model in a modelling step referred to as metamodelling. In metamodelling, the model reduction is obtained by considering only those processes and parameters for which the considered simulation output is sensitive or for which input data are available. As such, a simpler model can be obtained which encompasses the behaviour of the complex model and which is more compatible with available data bases. Regression analysis can be used to construct a metamodel (Figure A5-2).
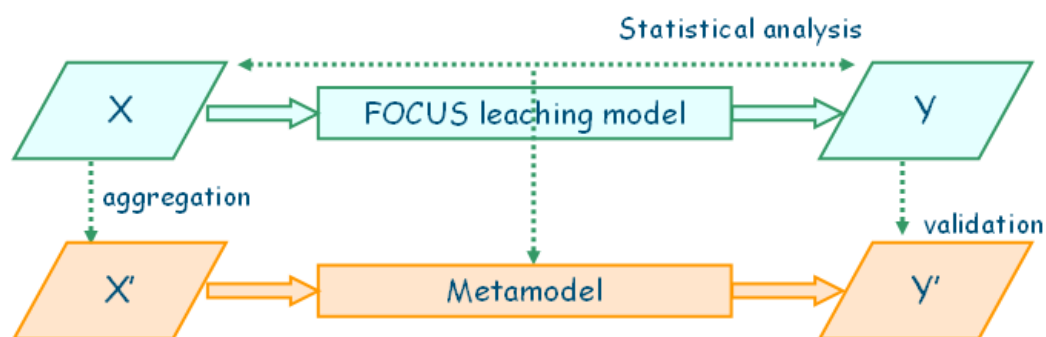
Figure A5-2. Metamodels are proxies of complex models.

The regression model can itself be a purely statistical model (Vanclooster et al., 2003; Stenemo et al., 2006; Piñeros Garcet et al., 2006) or a combination of a simplified process based model and a regression model (Van der Zee and Boesten, 1991; Stewart and Loague, 2004; Tiktak et al., 2006). The simplification of the model structure in a metamodel improves also the transparency of the model and is, therefore, easier to use within the communication process with non-technical stakeholders, in particular if a process-based metamodel is

proposed. Metamodelling theory and applications to emission modelling have recently been reviewed by Piñeros Garcet et al. (2006).

This appendix describes a tiered-approach to spatially-distributed modelling. In those cases where sufficient information for running a process based spatially distributed model is available, this model is used to derive spatial patterns of the leaching concentration directly (Figure A5-1). In other cases, metamodels are used to extend the simulations towards the entire intended use area. A single scenario is selected from the cumulative frequency distribution of the leaching map obtained with the metamodel. A FOCUS leaching model is run for this single scenario to get the regulatory endpoint.

This appendix is based on work reported in peer-reviewed scientific articles (Tiktak et al., 1996; 2002b; 2004; 2006). The backbone of the approach is spatially distributed versions of the FOCUS PEARL model, referred to as GeoPEARL and EuroPEARL. GeoPEARL and EuroPEARL results were used to calibrate a process-based metamodel (Van der Zee and Boesten, 1991). This metamodel was based on an analytical solution for piston flow. We use the metamodel of Van der Zee and Boesten (1991) in such a way that it describes concentrations instead of leached fractions and show how this metamodel can be used to assess the leaching risk at the national or at the European level.

The appendix starts with a general overview of the tiered approach (A5.2). Section A5.3 describes how to develop a spatially distributed leaching model, based on an existing FOCUS leaching model. Section A5.4 then shows how a metamodel of this spatially distributed model can be developed. In Section A5.5, both the metamodel and the numerical model are applied to the Netherlands. On the basis of this example, we will show that the metamodel gives comparable results as the original GeoPEARL model and that the results fit into the tiered assessment scheme. Section A5.6 provides the sensitivity of the metamodel to some basic model inputs. Section A5.7 reviews some of the uncertainties associated with the approach. General conclusions are given in Section A5.7.

A5.2 Overview of the method

A general overview of the proposed tiered-approach to spatially distributed modelling and calculating the regulatory endpoint is given in Figure A5-3.
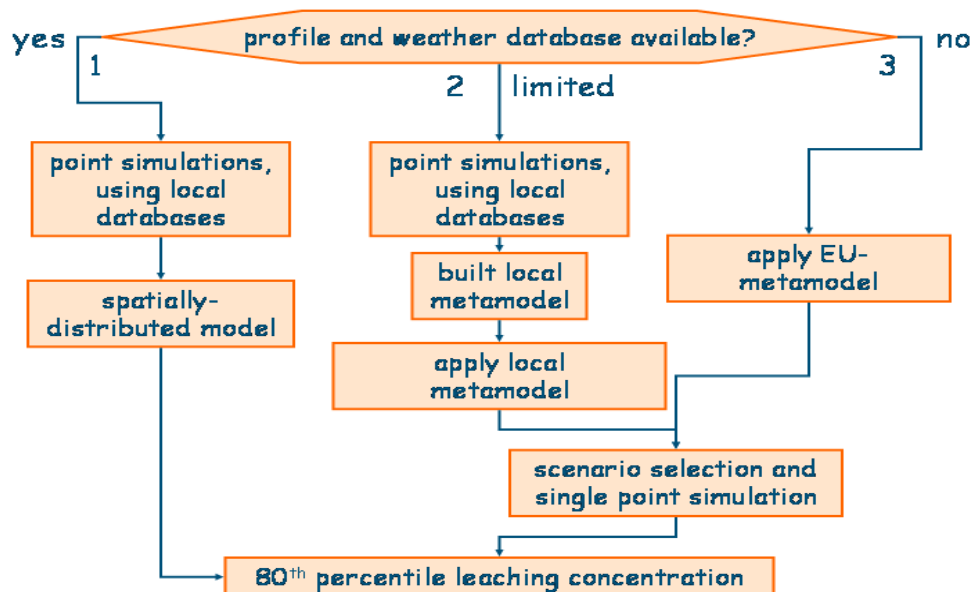
Figure A5-3. A tiered approach to spatially distributed modelling. The numbers refer to the pathways described in the text.

The diagram shows that there are in principle three pathways possible, depending on the availability of data:

1. If the soil profile and weather data cover the entire intended use area (and are considered of sufficient quality), then the regulatory endpoint can be calculated directly with a spatially distributed leaching model (Figure A5-1). An example of this approach is given by Tiktak et al. (2002b, 2003).

2. If the soil profile and weather data do not cover the entire intended use area, then a metamodel could be used to extend the simulations to the entire intended use area. A process based spatially distributed model is build, which does not cover the entire area. The model should be using local or national data bases, if possible. Then, a metamodel is build, using results from this model as a calibration dataset. The metamodel is then used to extend the simulations to the entire intended use area. An example of such an approach is given by Tiktak et al. (2006). A single scenario is selected from the cumulative frequency distribution of the leaching map generated by the metamodel, thereby accounting for the area of the intended use. A FOCUS leaching model is run for this single scenario to get the regulatory endpoint.

3. If there is no soil profile and weather data available from local or national inventories, then the EU-metamodel developed by Tiktak et al. (2006) can be used. This metamodel is applicable to the entire area of the EU and uses pan-European data bases. The reason is that the EU-metamodel is anticipated to perform also

328

reasonably well for national applications (see Section A5.5). The regulatory endpoint is calculated in the same way as in pathway 2.

If sufficient data are available, then pathway 1 (spatially distributed modelling) is likely to deliver the most realistic estimate of pesticide leaching in the intended use area. The efforts involved in developing and using a spatially distributed model are, however, also considerable. Pathway 3 is relatively easy to use – as shown later it comes down to the application of a single equation. Metamodelling, however, introduces an error in top of the original model, so the results may be less reliable than results obtained with the original model. For this reason, pathway 1 is the preferred option in those cases where sufficient data is available, and pathways 2 and 3 are the preferred options in all other cases. In view of this, the work group considers pathway 1 as a Tier 3 approach (Chapter 8) and pathway 2 and 3 as Tier 2b approaches (Section 7.2.5).

The most important elements of this tiered assessment scheme will be briefly described below. The appendix relies on the use of the PEARL and GeoPEARL models, but other FOCUS leaching models could have been used as well.

A5.3 Development of a spatially distributed pesticide leaching model

The development of a spatially distributed pesticide leaching model is described in Section 8.2.

A5.4 Metamodel development

A process-based metamodel (see pathway 2 of Figure A5-3) can be used to extrapolate simulations from a spatially-distributed model to the entire intended use area. The development of a metamodel consists of the following steps:
1. Selection of an appropriate metamodel
2. Derivation of the calibration dataset
3. Metamodel calibration (including an iterative step for optimising the metamodel)
4. Metamodel validation
5. Application of the metamodel to the intended use area
6. Selection of the target scenario

Step 1 Selection of an appropriate metamodel

Metamodelling concerns the approximation of a complex numerical model by a simple and faster model (see also the introduction of this appendix and Figure A5-2). Metamodels can roughly be grouped into two major categories (Janssen et al., 2005), i.e.

1. Purely statistical metamodels. The original model is executed several times and regression techniques are used to describe the relation between model inputs and model outputs. Statistical metamodels are black-boxes – no physical knowledge of the system is included. An overview of regression techniques that can be used is listed in Chambers and Hastie et al. (1991) and Janssen et al. (2005). They differ from simple multiple (linear or polynomial) regression models to advanced statistical techniques like kriging and artificial neural networks. Rather good approximations of pesticide leaching models have recently be obtained with artificial neural networks (Vanclooster et al., 2003; Stenemo et al., 2006), because they outperform other regression methods in terms of flexibility and versatility. The disadvantages of artificial neural networks are, however, that a large number of model runs is required (usually more than 100,000), that artificial neural networks can easily be over parameterised leading to non-uniqueness.

2. Process based metamodels. This kind of models tries to describe the most important processes in a simple, but process oriented way. Many authors have used analytical models or impulse response functions for this purpose. The best known models of this type are the attenuation factor (Loague et al., 1989; 1996, Loague and Corwin, 1996) and the transfer function (Jury and Roth, 1990; Stewart and Loague, 2003, 2004). Analytical models do not account for vertical heterogeneity and assume steady-state conditions, so that they may not be compatible with results from numerical models. This problem can be overcome by introducing effective model parameters (Van der Zee and Boesten, 1991), which need to be calibrated against results form a numerical model. Van der Zee and Boesten (1991) fitted results from one scenario only, so that the obtained effective model parameters might not be applicable to the entire intended use area. Tiktak et al. (2006) build upon this approach by fitting a large number of scenarios simultaneously. In this way, a process-based metamodel of GeoPEARL resulted.

As shown in the literature, good model approximations can be obtained with either of the two model types. However, due to the non-linear character of pesticide leaching models, advanced statistical techniques like artificial neural networks are required if a purely statistical model is used (Vanclooster et al., 2003; Stenemo et al., 2006; Piñeros Garcet et al., 2006). For this reason, we recommend the use of process-based metamodels. In

contrast to complex statistical models like artificial neural networks, these models have a simple and transparent structure which can be easily communicated to non-technical stakeholders.

In the rest of this section, a process-based metamodel of EuroPEARL, referred to as MetaPEARL is described. The aim of this metamodel was to predict the vulnerability to pesticide leaching at the scale of the EU (Tiktak et al., 2006). The metamodel has been developed to monitor the progress of the Thematic Strategy on the Sustainable Use of Pesticides, but it is available for use within FOCUS as well.

Being in line with the FOCUS definition of obtaining the 90[th] overall percentile in space and time the target variable of the metamodel was the 80[th] percentile of the leaching concentration at 1 m depth in time from a long time series of simulation runs with different weather, but another percentile can be chosen as well. The metamodel considers an analytical solution of the mass fraction of a pesticide dose that leaches below a certain depth in a homogeneous system, based on (i) the convection-dispersion equation (ignoring diffusion), (ii) steady-state water flow, (iii) a linear adsorption isotherm, and (iv) first-order degradation kinetics. Jury and Gruber (1989) derived this solution and their equation can be rewritten as:

$$F = \exp\left(-\frac{L}{2L_{dis}} \left(\sqrt{1 + \frac{4\mu L_{dis}(\theta + \rho f_{om} K_{om})}{q}} - 1 \right) \right) \tag{A5-1}$$

in which F (-) is the mass fraction leached, L (m) is the depth considered, L_{dis} (m) is the dispersion length, μ (d^{-1}) is the first-order degradation rate coefficient, θ ($m^3 m^{-3}$) is the volume fraction of water, ρ (kg dm^{-3}) is the dry bulk density of the soil, f_{om} (kg kg^{-1}) is the organic matter content, K_{om} ($dm^3 kg^{-1}$) is the coefficient for distribution over organic matter and water, and q (m d^{-1}) is the volume flux of water.

According to its definition, the leaching concentration is a flux concentration. Jury and Roth (1990) describe the solution for the flux concentration, on which Equation A5-1 is based. Their equations 2.17, 2.51 and 4.68 indicate that this solution is given by:

$$C_L = \frac{ML}{2q \frac{t}{R} \sqrt{\pi q L_{dis} \frac{t}{R}}} \exp(-\mu t) \exp\left(\frac{-\left(L - \frac{qt}{\theta R}\right)^2}{4q L_{dis} \frac{t}{R}} \right) \tag{A5-2}$$

in which C_L (kg m^{-3}) is the flux concentration at the lower boundary, M (kg m^{-2}) is the pesticide dose, t (d) is the time, and R (-) is the retardation factor, which is defined by:

$$R = 1 + \frac{\rho}{\theta} f_{om} K_{om} \qquad\qquad\qquad\qquad (A5\text{-}3)$$

For pesticide leaching, one may expect that the flux concentration evaluated at a certain depth in soil is more or less proportional to the fraction of the dose that leaches beyond that depth: low fractions leached can only be achieved by low leaching concentrations and similarly high fractions leached can only be achieved by high leaching concentrations. We made Monte Carlo simulations with Equation A5-1 and assumed uniform distributions for θ, R, q, and the half-life of the pesticide. The range of θ was 0.1–0.3 $m^3 m^{-3}$; the range of R was 1–100; the range of q was 0.25–2.5 mm d^{-1}, and the range of the half-life was 20–100 d. The pesticide dose was 1 kg ha^{-1}, the depth in soil was 1 m, and the dispersion length was 0.05 m. For each combination of the stochastic variables the maximum in time of the concentration was calculated and compared with the fraction leached from Equation A5-1. Figure A5-3 shows that the maximum concentration is indeed more or less directly proportional to the fraction leached. This suggests that the metamodel for the 80[th] percentile concentration can be based on the simpler equation for the fraction leached.

Van der Zee and Boesten (1991) adapted Equation A5-1 slightly to include also pesticide uptake by plant roots:

$$F = \exp\left(-\frac{L}{2L_{dis}} \left(\sqrt{1 + \frac{4\mu L_{dis}(\theta + \rho f_{om} K_{om}) + 4gSL_{dis}}{q}} - 1 \right) \right) \qquad (A5\text{-}4)$$

where g (-) is the transpiration stream concentration factor and S (d^{-1}) is the water uptake by plant roots. Van der Zee and Boesten (1991) made calculations with a model similar to PEARL for a single Dutch soil (L_{dis} = 0.05 m), but for a range of degradation half-lives and K_{om}-values. They fitted the fraction leached to Equation A5-4 with θ, S, and q as regression parameters. They found that Equation A5-4 was a suitable metamodel to describe the output of the simulation model. Moreover, they found that the fitted values of θ, S and q were physically realistic.
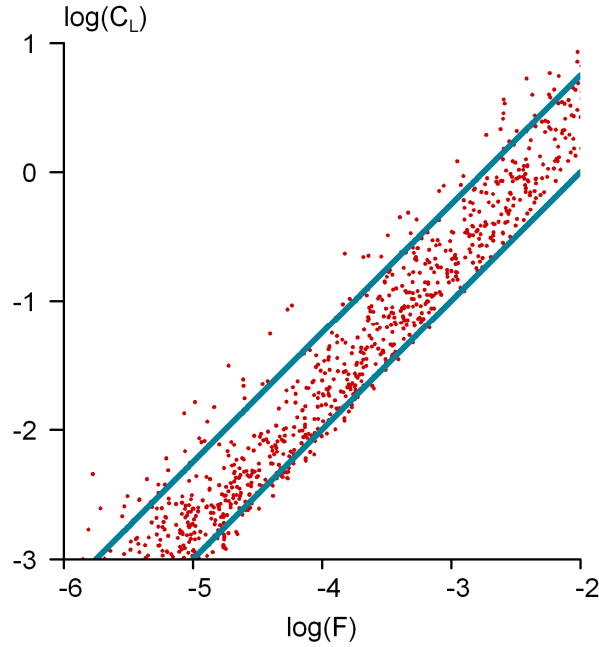
Figure A5-4. **The maximum in time of the flux concentration at 1 m depth (µg L^{-1}) as calculated with Equation A5-2 as a function of the leached fraction (C_L) as calculated with Equation A5-1. The points are Monte Carlo calculations based on random values for the volume fraction of water, retardation factor, water flux and half-life of the pesticide.**

Van der Zee and Boesten (1991) used also the fraction leached for the same system, but now assuming piston flow instead of the convection-dispersion equation:

$$F = \exp\left(-\frac{\mu(\theta + \rho f_{om} K_{om})L + gSL}{q} \right) \tag{A5-5}$$

They fitted the calculated fractions leached also to Equation A5-5 using again θ, S, and q as adjustable parameters. Equation A5-5 appeared to describe the calculated fractions equally well as Equation A5-4, but the fitted value of q was less realistic. Van der Zee and Boesten (1991) attributed this to the fact that Equation A5-5 ignores dispersion and thus the fitted values of q include the effect of the dispersion process.

For our metamodel we prefer an equation of the type of Equation A5-5 over an equation of the type of Equation A5-4, because Equation A5-4 describes the calculated fractions equally well with fewer parameters (a metamodel should be as simple as possible by its nature). So we combine Equation A5-5 with the phenomenon that the flux concentration is approximately directly proportional to the fraction leached (Figure A5-4). This gives the following metamodel for the 80th percentile leaching concentration:

$$C_L = C_0 \exp\left(-\frac{\mu(\theta + \rho f_{om} K_{om})L + gSL}{q} \right) \tag{A5-6}$$

where C_0 (kg m^{-3}) is the concentration at the upper boundary of the column.

One cannot expect that Equation A5-6 gives as accurate predictions of leaching concentrations as a model such as GeoPEARL, which accounts for vertical heterogeneity of soil physical and chemical properties, non-linearity in sorption, daily variations of water fluxes, etcetera. Therefore, we rewrote Equation A5-6 as a multiple linear regression model and fitted the leaching concentration to the leaching concentration obtained by GeoPEARL:

$$\ln C_L = \alpha_0 - \alpha_1 X_1 - \alpha_2 X_2 - \alpha_3 X_3 \qquad (A5-7)$$

in which α_0, α_1, α_2, and α_3 are the regression coefficients and where X_1 (-), X_2 (-), and X_3 (-) are independent regression variables, which are defined as follows:

$$X_1 = \frac{\mu \theta L}{q} \qquad (A5-8)$$

$$X_2 = \frac{\mu \rho f_{om} K_{om} L}{q} \qquad (A5-9)$$

$$X_3 = \frac{gSL}{q} \qquad (A5-10)$$

Rewritten in this way, a process-based metamodel of GeoPEARL results.

Step 2. Derivation of the calibration dataset
Data are needed for metamodel calibration and for metamodel application. The following general guidelines can be given:

- Parameters for the calibration data set must be inferred from the same data base as the data base used for the process-based model. As mentioned in Section A5.3, full spatial coverage is not required, but the spatially distributed model must be sufficiently representative for the intended use area.
- Parameters for metamodel application must cover the entire intended use area. Otherwise, the calculation of spatial percentiles would be impossible. Parameters can be derived from different data bases.

Below follows a description how the calibration data set for a pan-European metamodel based on EuroPEARL was developed. This description can be seen as an example; the derivation of a calibration dataset based on local or national data bases should be done in a corresponding way. The derivation of a data set for metamodel application is described in step 4.

The EuroPEARL data base is sufficiently representative for conditions in Europe (Section A5.3), so this model can be used to parameterize a metamodel for the entire EU. To assure

that the metamodel also covers a wide range of substances, EuroPEARL runs have to be done for a wide range of substances. Tiktak et al. (2006) constructed a set of 56 example pesticides from a grid in the DegT50/K_{om}-parameter plane. The calculations were made assuming a single application of 1 kg/ha to two different crops (maize and winter cereals) grown in monoculture. The pesticides were annually applied to the soil surface, one day after crop emergence. The degradation half-life (DegT50) ranged from 10 to 200 days and the organic matter-water partition coefficient (K_{om}) was between 0 and 200 dm^3 kg^{-1}. The 56 combinations of *DegT50* and K_{om} cover the full range of relevant pesticides as described by Boesten and van der Linden (1991). Because the number of unique combinations in EuroPEARL amounts to 1062, the number of PEARL runs amounted to 59,808 (1062x56). EuroPEARL is rather demanding with respect to computer resources, so we used a computer cluster consisting of 256 loosely coupled CPU's to perform the simulations. This assured that the simulations could be done within 2 days.

For each PEARL run, the independent regression variables $X_1..X_3$ in Equations A5-8, A5-9, and A5-10 must be calculated as well. These equations contain two substance parameters (μ and K_{om}), two soil parameters (ρ and f_{om}), three dynamic soil parameters (θ, *S* and *q*), and two constants (*L* and *g*). As mentioned above, the parameters must be inferred from the same data base as used for the parameterization of the spatially distributed model, which in this case is the EuroPEARL data base. In the case of dynamic properties, 20-years averages should be taken (the simulation length excluding the warm-up years). In the case of depth-dependent soil properties, averages for the top 1 m (the target depth) should be calculated, using the horizon thickness as a weighing factor. The degradation rate coefficient, μ, is not directly available in the EuroPEARL data base, because it is temperature dependent. The Arrhenius equation should be applied to account for this effect:

$$\mu = \exp\left(\frac{-E_a}{R}\left(T^{-1} - T_r^{-1}\right)\right)\frac{\ln(2)}{DegT_{50}} \tag{A5-11}$$

where *DegT50* (d) is the degradation half-life at reference temperature, E_a (J mol^{-1}) is the molar activation energy, R (J mol^{-1} K^{-1}) is the molar gas constant, *T* (K) is the 20-years average air temperature and T_r (K) is the temperature at reference conditions, which was set to 20 °C. The molar activation energy should be fixed to the same value as used for the PEARL calculations.

The organic matter content, f_{om}, must be averaged over the top 1 m, using the horizon thickness as a weighing factor. The bulk density of the soil must be calculated in exactly the same way as done in the original model. EuroPEARL uses a continuous pedotransfer approach to relate the bulk density, ρ (kg dm^{-3}), to the organic matter content, so this

approach should be used when building a metamodel based on EuroPEARL simulations (Tiktak et al., 1996):

$$\rho = 1.80 + 1.24 f_{om} - 2.91\sqrt{f_{om}} \qquad (R^2 = 0.91) \qquad \text{(A5-12)}$$

Figure A5-5 shows the basic maps that were available for the EuroPEARL model.

Dynamic properties (θ and S) should also be taken from the output files of the spatially distributed model. These parameters should first be averaged over the top 1 m of the soil and then averaged over the 20-years simulation period. The water flux, q, can be represented by the excess rainfall over evapotranspiration and run-off.

The time of application has an important effect on the spatial patterns of pesticide leaching. Therefore different metamodels should be constructed for spring applied and for autumn applied pesticides. In practice, this implies that the entire exercise needs to be done two times.
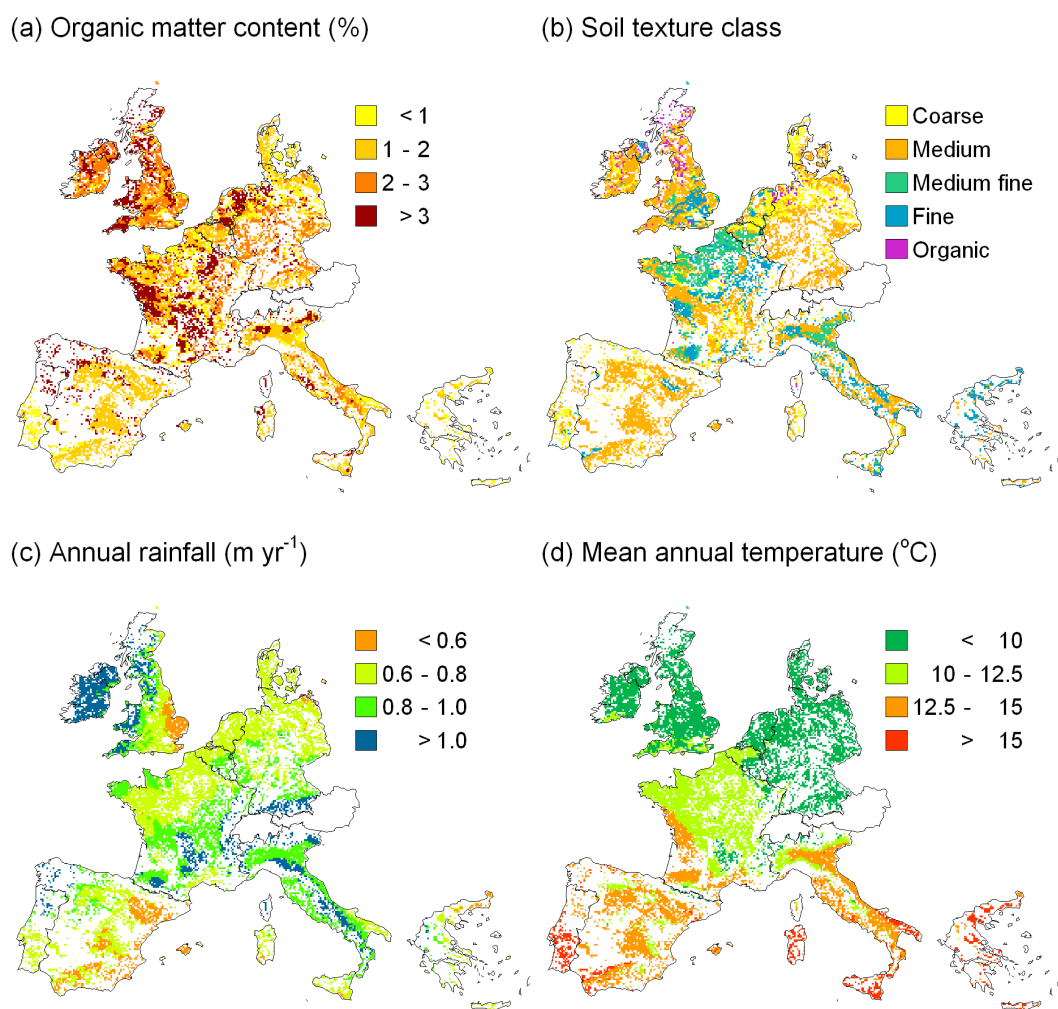
Figure A5-5. Basic maps for EuroPEARL. Areas without agricultural land-use and areas where insufficient soil information was available, are not shown. (a) Organic matter content of the upper meter as derived from the SPADE data base; (b) soil texture from the 1:1,000,000 Soil Map of Europe; (c) mean annual rainfall, and (d) mean annual temperature. Temperature and rainfall were taken from the Pan-European climate data base.

Step 3 Metamodel calibration

The actual fitting of the metamodel can be done in a standard statistical package. Ordinary regression techniques are extremely vulnerable to outliers. For this reason, it is recommended to use robust regression algorithms. Robust regression techniques generate answers similar to the classical least-squares regression when the data are linear with normally distributed errors, but differ significantly from the least-squares fit when the data contain significant outliers. Tiktak et al. (2006) obtained reasonable results with the robust *MM*-regression algorithm, available in *SPlus* (Yohai and Zamar, 1997).

337

In the remainder of this section, the metamodel calibration done by Tiktak et al. (2006) is summarized. They fitted two metamodels, i.e. one for a spring-applied pesticide ('leaching set spring') and one for an autumn applied pesticide ('leaching set autumn'). Based on this example, the following general recommendations can be given for metamodel calibration:

- the third term of Equation A5-7 (the plant-uptake term) should not be used, because this yielded physically unrealistic values.
- if the metamodel is intended to be used throughout different major climatic zones, different metamodels parameterizations should be used for each individual climatic zone (i.e. the calibration dataset should be split based on these zones). For pan-European leaching assessments, four climatic zones were sufficient (Table A5-1).

Table A5-1. Major climate zones of the European Union, based on mean annual rainfall and mean annual temperature. Zones are a reclassification of the zones described in FOCUS (2000).

Zone ID	Mean annual rainfall (m yr^{-1})	Mean annual temperature (^{o}C)
Temperate, dry (TD)	< 0.8	< 12.5
Temperate, wet (TW)	> 0.8	< 12.5
Warm, dry (WD)	< 0.8	> 12.5
Warm, wet (WW)	> 0.8	> 12.5

Tiktak et al. (2006) optimised the metamodel in different calibration steps (called Model I, II and III) and obtained a recommended version (Model III) (see Table A5-2)

Table A5-2. Coefficients resulting from calibration of the metamodel to the two leaching sets.

Model[†]	Leaching set	Region[‡]	α_0 [***]	α_1	α_2	α_3	R^2 [*]
Model I	Autumn	EU-15	4.10 (0.005)[**]	0.21 (0.001)	0.58 (0.000)	-2.64 (0.217)	0.97
	Spring	EU-15	3.80 (0.005)	0.48 (0.001)	0.53 (0.000)	-2.37 (0.109)	0.97
Model II	Autumn	EU-15	4.95 (0.004)	0.07 (0.002)	0.58 (0.001)	NA[§]	0.94
	Spring	EU-15	4.76 (0.005)	0.39 (0.003)	0.51 (0.001)	NA	0.90
Model III	**Autumn**	**TD**	**5.30 (0.006)**	**0.16 (0.002)**	**0.46 (0.001)**	**NA**	**0.97**
		TW	**4.95 (0.004)**	**0.16 (0.003)**	**0.60 (0.001)**	**NA**	**0.97**
		WD	**5.20 (0.011)**	**0.07 (0.002)**	**0.37 (0.001)**	**NA**	**0.95**
		WW	**5.02 (0.008)**	**0.23 (0.004)**	**0.57 (0.001)**	**NA**	**0.98**
	Spring	**TD**	**5.09 (0.007)**	**0.44 (0.003)**	**0.46 (0.001)**	**NA**	**0.95**
		TW	**4.72 (0.006)**	**0.39 (0.004)**	**0.58 (0.001)**	**NA**	**0.96**
		WD	**5.07 (0.018)**	**0.28 (0.004)**	**0.30 (0.002)**	**NA**	**0.91**
		WW	**4.81 (0.002)**	**0.58 (0.007)**	**0.46 (0.002)**	**NA**	**0.97**

† Model I: model based on Equation A5-7; Model II: model based on Equation A5-7 with α_3 fixed to zero; Model III: model based on Equation A5-7 with α_3 fixed to zero and with dataset split into climate zones. See further text.

‡ TD: Temperate and Dry; TW: Temperate and Warm; WD: Warm and Dry; WW: Warm and Wet; EU-15: European Union without the new member States. See further Table A5-2.

§ Not applicable

* Robust version of R^2 as described by Yohai and Zamtar (1997).

** Figures in parentheses denote standard errors

*** α_0, α_1, α_2, and α_3 are regression coefficients (Equation A5-8).

They first fitted a metamodel including the plant uptake term (X_3). The coefficients for the third term were, however, physically unrealistic (Table A5-2). The regressions were therefore repeated for a model with two regression variables, namely X_1 and X_2. Results are also shown in Table A5-2 (Model II). All coefficients of Model II are physically realistic (i.e., positive), while the proportion of variation explained by the metamodel is still high. The most important difference between the two leaching sets is in α_1, which is lower in the case of autumn applied pesticides. The X_1 term of Equation A5-7 reflects the retardation of solute resulting from the volume fraction of water in soil (it is the θ-term of the retardation factor), while the X_2 term reflects the retardation resulting from sorption. Apparently, sorption is the key factor for the leaching concentration in the case of autumn applied pesticides. A possible explanation is that autumn applied pesticides become only subject to degradation if the residence time in the topsoil is long enough: directly after application, the temperature is low and degradation rates are small.

Model II was used to construct Figures A5-6a and A5-6b. These figures show the leaching concentration predicted by EuroPEARL as a function of the leaching concentration predicted

by the metamodel. The number of leaching points in each figure equals 59,808. The concentrations were plotted on a log10-scale and the lines represent the fit. The figure shows that, despite the high proportion of variation explained by the metamodel (Table A5-2), there is large scatter around the 1:1 line. Further inspection of the leaching sets suggests that the deviation from the 1:1 line is related to the annual precipitation: under dry conditions, the metamodel tends to underestimate the leaching concentration, whereas the leaching concentration is overestimated in those cases where the mean annual precipitation is high.

To reduce the systematic differences due to climate, the leaching sets were split in four subsets, namely one for each climate zone in Table A5-2. The underlying assumption is that the climate zones are more homogeneous with respect to seasonal dynamics of weather than Europe as a whole. Figures A5-9c and A5-6d show that the systematic errors are indeed reduced. The regression coefficients as shown in Table A5-2 (Model III) are generally low in dry climate zones and high in wet climate zones: α_1 increases in the order WD < TD $\approx$ TW < WW, while coefficient α_2 increases in the order WD < TD < TW $\approx$ WW. This suggests that in the case of dry climates, the effective model parameters deviate more from realistic values than in the case of wet climates. Averaging causes bias in the results of the analytical model, which is reflected in the coefficients of the metamodel. The effect of averaging is expected to be more pronounced in the case of dry climates, because the seasonal variability of the water flow pattern is generally higher in those climates. Van der Zee and Boesten (1991) found that the bias between realistic and effective model parameters appears most in the water flow velocity. They attributed this to the fact that Equation A5-5 ignores dispersion and thus the fitted values of q include the effect of the dispersion process. Using their findings, one can make an estimation of the ratio between the true water flow velocity and the apparent water flow velocity for the four climate zones by substituting α_1 and α_2 into Equations A5-7 to A5-9. The calculated ratios (approximately two for wet climates and four for dry climates) confirm that the effect of averaging is most pronounced in the dry climate zones. Notice that the above exercise yields only a crude estimate of the apparent flow velocity, because the averaging of the degradation rate (μ) and the non-linearity of the sorption process affects the leaching as well.

Summarizing, one can state that the time of application mainly affects the ratio between α_1 and α_2, while the absolute values are affected mainly by the seasonal dynamics of water flow (represented here by the climate zone). We can conclude that Model III explains a high proportion of variation of the original model, while also adequately describing the dependency of the leaching concentration on the main processes, i.e., retardation,

degradation, and hydrology. Hence, we can use Model III to map the leaching concentration at the European level.

Step 4 Metamodel validation

The aim of the metamodel is to find a scenario that represents the target vulnerability. Therefore the spatial patterns of ground water vulnerability predicted by the metamodel must show a good correspondence to the ground water vulnerability predicted by the numerical model. Comparison of the spatial patterns predicted by the metamodel with the spatial pattern predicted by the numerical model is therefore an essential part of the validation of the metamodel. The following general guidelines can be given for metamodel validation:

- To avoid possible biases due to the use of different data sets, <u>the metamodel should be validated using the same data set as the original model</u> (otherwise comparison of spatial patterns is impossible). If the original model does not cover the entire intended use area, this implies that the metamodel validation is limited to the area for which data are available in the original model (see example below).
- Both <u>visual and quantitative techniques</u> should be used for metamodel validation.

Notice that the validation is limited to comparing the spatial patterns of ground water vulnerability. The final aim of a Tier 2b assessment is to calculate the leaching concentration with a FOCUS ground water model for a single use-specific scenario (see Sections 7.2.5 and A5-2). The validation of these use-specific scenarios requires that also the procedures for selecting these scenarios must be validated. See further Section A5.5.
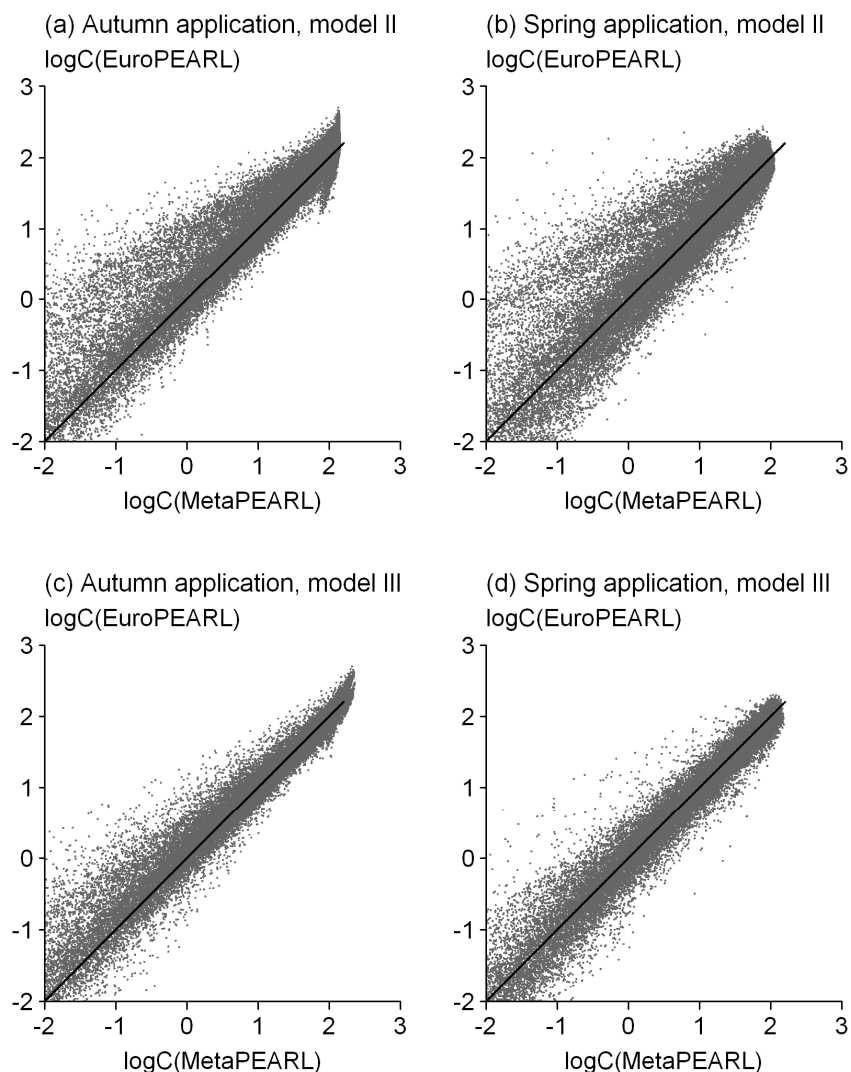
Figure A5-6. Leaching concentration C_L (µg L^{-1}) at 1 m depth as calculated with EuroPEARL plotted against leaching concentrations predicted with the metamodel (Equation A5-5). The points are leaching concentrations and the line represents a 1:1 correspondence. Model II: one regression for the EU-15 as a whole. Model III: regressions for individual climatic zones as described in Table A5-2.

To demonstrate how the validation could be carried out, the work by Tiktak et al. (2006) is summarized. They used EuroPEARL and Metamodel III (Table A5-2) to generate maps of the leaching concentration at 1 m depth, which is the compliance depth for the first-tier of the European pesticide registration procedure (FOCUS, 2000). As described before, they mapped the 80[th] percentile of the leaching concentration due to weather conditions. To avoid possible bias that might result from using different datasets, they applied the metamodel to the same data set as used for the parameterization of EuroPEARL; the most important soil and climate properties are shown in Figure A5-5. The comparison was done for three

example substances as described in FOCUS (2000). A summary of the most important
pesticide properties is given in Table A5-3.

Table A5-3. Overview of the most important properties of the pesticides considered in this study.

Property[†]	Substance		
	A	**B**	**D**
M (g mol^{-1})	300	300	300
$P_{v,s}$ (Pa)	0	0[‡]	0
S_w (mg L^{-1})	90	90	90
K_{om} (dm^3 kg^{-1})	60	10	35
$DegT50$ (d)	60 (20^{o}C)	20 (20^{o}C)	20 (20^{o}C)

† M is molar mass, $P_{v,s}$ is the saturated vapour pressure, S_w is the solubility in water, K_{om} is the coefficient of equilibrium sorption on organic matter, and $DegT50$ is the degradation half-life under reference conditions.

‡ Parameter value differs slightly from value given in FOCUS (2000).

The comparison was done with a combination of qualitative (visual) methods and quantitative methods. Quantitative methods try to express the agreement in performance criteria, while qualitative methods are based on subjective visual methods. The performance criteria were selected in order to reflect the objectives of the metamodel, namely the ability to predict the leaching concentration at multiple sites and the ability of the metamodel to predict the target variable for European registration procedures. The target variable is defined as the 80th percentile leaching concentration in a FOCUS period at an 80th percentile vulnerable grid cell (i.e., 80% of the area of the European Union has a lower leaching concentration than the grid cell). The three selected indicators are the Normalized Average Error (NAE), the Normalized Root Mean Square Error ($NRMSE$), and the Model Efficiency (ME). The NAE measures the bias in the target variable, which is the difference between the metamodel predictions and the EuroPEARL 'observations'. The $NRMSE$ measures the deviation between the predicted and 'observed' leaching concentrations. T he Modelling Efficiency quantifies the improvement of the metamodel over the mean of the EuroPEARL 'observations'. Any positive value of ME can be interpreted as an improvement compared to a spatial averaged concentration over Europe as calculated with EuroPEARL. A value of 1 is best. The indicators are defined as:

$$NAE = \frac{P_{80} - O_{80}}{O_{80}}$$
(A5-13)

$$NRMSE = \frac{\frac{1}{N}\sqrt{\sum_{i=1}^{N}(P_i - O_i)^2}}{\overline{|O|}} \tag{A5-14}$$

$$ME = \frac{\left(\sum_{i=1}^{N}(O_i - \overline{O})^2 - \sum_{i=1}^{N}(P_i - O_i)^2\right)}{\left(\sum_{i=1}^{N}(O_i - \overline{O})^2\right)} \tag{A5-15}$$

where P_i and O_i denote the predicted and observed value in grid cell i, respectively, $\overline{P}$ and $\overline{O}$ are the mean values, P_{80} and O_{80} are the 80th percentiles of the leaching concentrations in the maps, and N is the number of grid cells.

Maps of the predicted leaching concentration are shown in Figure A5-7 (autumn applications) and Figure A5-8 (spring applications). The maps generated by EuroPEARL and the maps generated by Metamodel III show a striking similarity. Both models simulate in a consistent way higher leaching concentrations in response to autumn applications, which was expected. Differences between autumn applications and spring applications are also generally higher in southern Europe, where there is a distinct dry and hot season (see explanation in the previous section). The two models also consistently predict that the leaching concentration increases in the order Substance D < Substance A < Substance B. Despite the similarity between the maps, there are also regions where there are significant differences. In Denmark and north eastern Germany, for example, the metamodel predicts lower leaching concentrations than EuroPEARL, while the opposite is true for the Netherlands. Analysis of the SPADE data base showed that the soil profiles in Denmark and Germany are more heterogeneous with respect to the vertical distribution of organic matter than the average profile, while the opposite is true for the Netherlands. The phenomenon that the leaching concentration is underestimated when vertical heterogeneity is underestimated is line with earlier findings reported by Tiktak et al. (2002a).

Predicted leaching concentration (autumn application)
(a) Substance A, EuroPEARL   (b) Substance A, Metamodel III
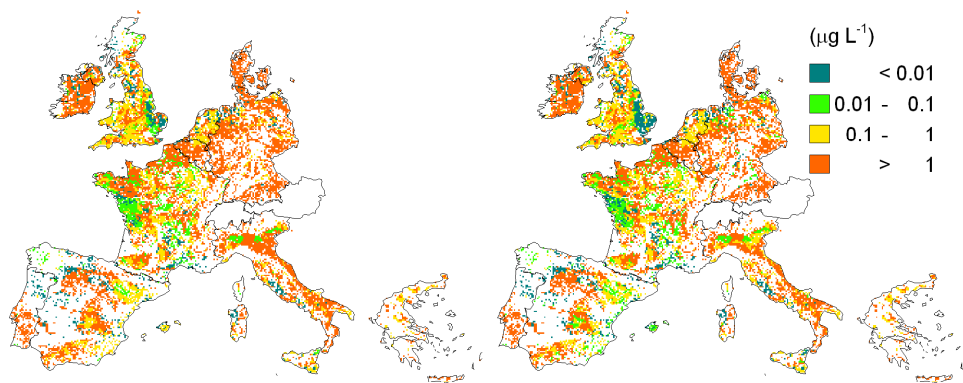
(c) Substance B, EuroPEARL   (d) Substance B, Metamodel III
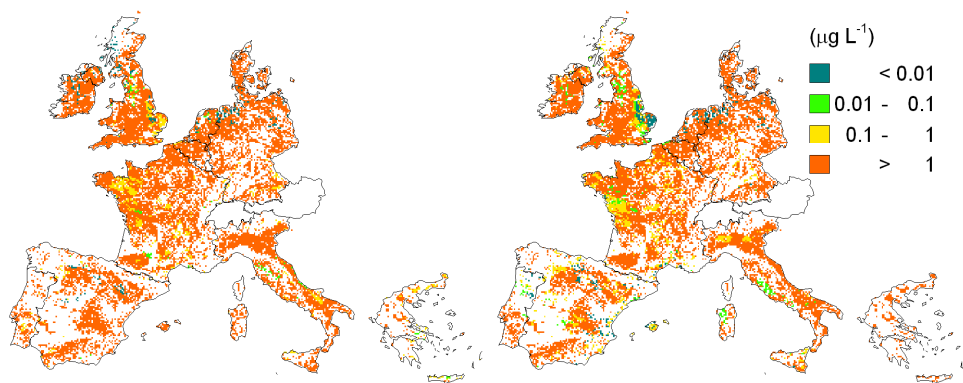
(e) Substance D, EuroPEARL   (f) Substance D, Metamodel III
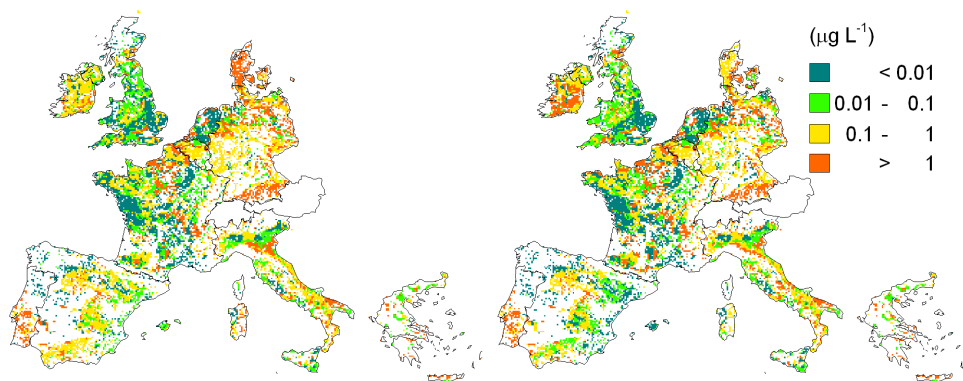
Figure A5-7. Predicted leaching concentration in response to annual applications in autumn, as calculated with EuroPEARL (left) and the metamodel (right). Areas without agricultural land-use and areas where EuroPEARL could not be parameterized are not shown.

Predicted leaching concentration (spring application)
(a) Substance A, EuroPEARL (b) Substance A, Metamodel III
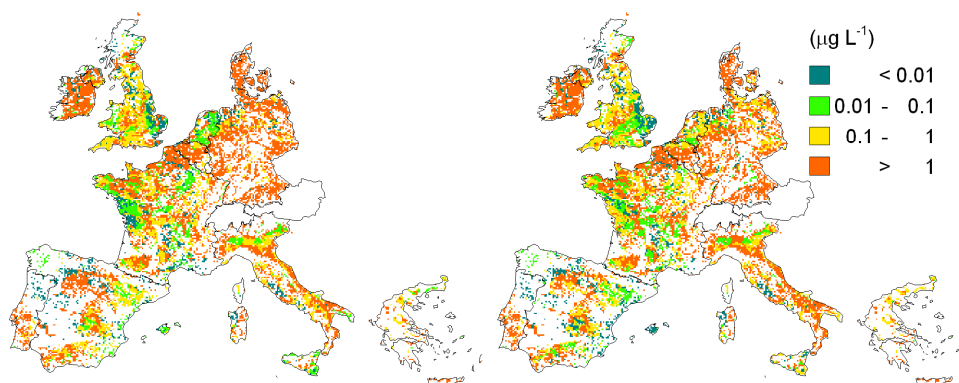
(c) Substance B, EuroPEARL (d) Substance B, Metamodel III
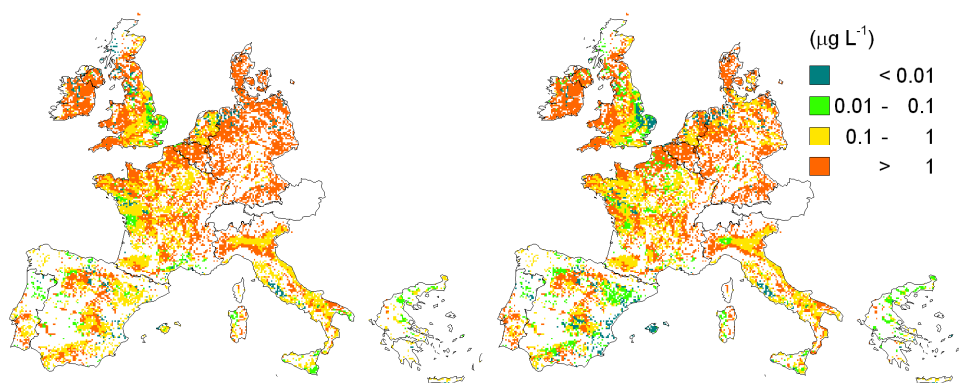
(e) Substance D, EuroPEARL (f) Substance D, Metamodel III
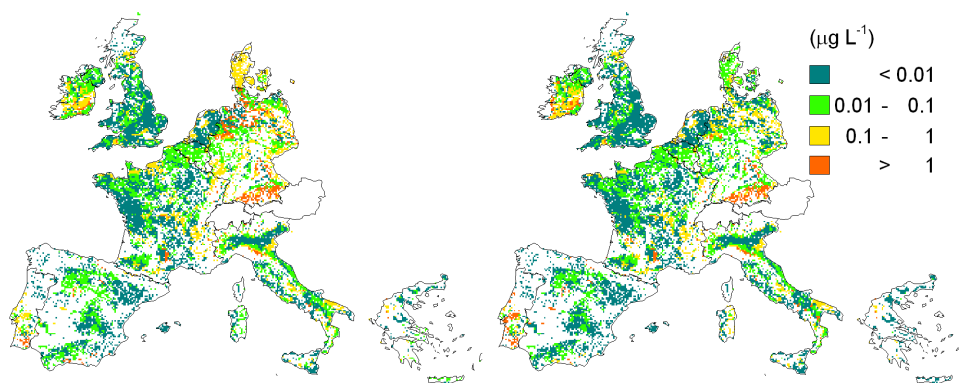
Figure A5-8. Predicted leaching concentration in response to annual applications in spring, as calculated with EuroPEARL (left) and the metamodel (right). Areas without agricultural land-use and areas where EuroPEARL could not be parameterized are not shown.

The performance criteria are listed in Table A5-4. Using the classification proposed by Henriksen et al. (2003), the *ME* scores 'excellent' for Substances A and D, and 'good' for

Substance B. Table A5-3 shows that Substance B has a lower sorption coefficient than Substances A and D. Apparently, the metamodel performs better for non-mobile substances. This was expected because short-term variations due to weather conditions are attenuated in the case of substances with a high K_{om}. The *NRMSE* is generally lower than 10%. Highest values are found for Substance D. This was also expected. Substance D has the lowest leaching potential, and the scatter around the 1:1 line increases at low concentration ranges (Figure A5-6). The 80[th] percentile of the leaching concentration is best predicted for Substance A. The largest error is found for Substance D applied in spring, which confirms results shown in the maps (Figure A5-8).

Table A5-4. Summary of Metamodel III performance indicators (-).

Substance	Spring application			Autumn application		
	ME†	*NRMSE*	*NAE*	*ME*	*NRMSE*	*NAE*
A	0.892	0.022	-0.023	0.917	0.016	-0.035
B	0.643	0.039	0.047	0.676	0.017	-0.181
D	0.875	0.085	-0.409	0.934	0.040	0.172

† *ME*: Modelling Efficiency; *NRMSE*: Normalized Root Mean Square Error; *NAE*: Normalized Absolute Error

Both the visual inspection of the leaching maps and the quantitative indicators reveal that the performance of the metamodel is generally good. The performance indicators also show, however, that the application of the metamodel should be done with care.

Step 5: Metamodel application to the entire intended use area
The final product of the metamodel is a map showing the ground water vulnerability of the entire intended use area. If the original model does not cover the entire intended use area, a different dataset must be used for metamodel application. The availability of sufficient soil profile data is often the limiting factor, so the metamodel parameterisation scheme should preferably avoid the use of a soil profile data base. Tiktak et al. (2006) mapped ground water vulnerability for the entire area of the EU with a resolution of 10x10 km^2. They suggest using the parameterisation scheme as shown in Figure A5-9.
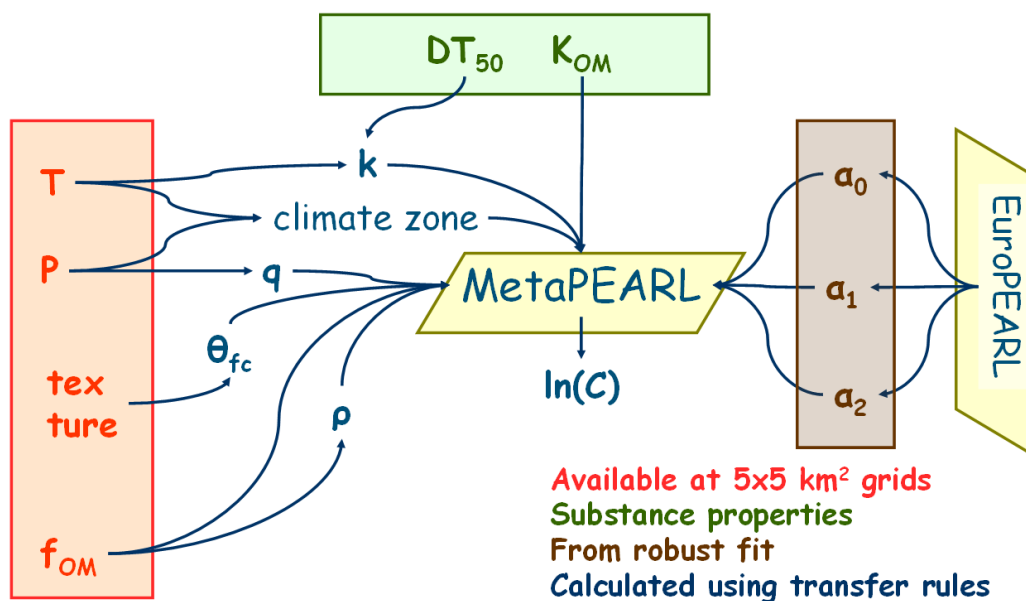
Figure A5-9. Parameterization scheme for MetaPEARL. The final metamodel uses only four independent spatially distributed model inputs.

The following spatially distributed model input parameters are required for MetaPEARL:

- The transformation rate coefficient, μ, should be calculated with Equation A5-11. The temperature is taken from the MARS data base, which contains a map of the long-term average temperature based on data from 1500 weather stations (Vossen and Meyer-Roux, 1995).

- The flux at 100 cm depth, q_{100}, can be calculated from the mean annual precipitation using the regression in Figure A5-10a. The regression was carried out on data in the EuroPEARL output files. There appeared to be a strong correlation between mean annual precipitation and the flux at 100-cm depth. This strong correlation was expected, because mean actual evapotranspiration rates show limited variability throughout Europe (Roberts, 1983). The mean annual precipitation is taken from the MARS data base (see above).

- The long-term average soil water content can be approximated by the water content at field capacity (f_c), which is obtained from soil texture using pedotransfer rules (Jamagne et al., 1995). Analysis of the EuroPEARL output files revealed that the long-term average soil water content was generally within 5% of the water content at field capacity, so this is a realistic approximation (Figure A5-10b).

- The organic matter content should be taken from the European organic matter map (Jones et al., 2004; 2005).

- The bulk-density should be calculated from the organic matter content using a continuous pedotransfer function Equation A5-11.

Parameterized in this way, the metamodel uses therefore only four independent spatially-distributed model inputs (organic matter, texture, annual precipitation, and mean annual temperature). These four parameters are available in georeferenced data bases that cover the entire area of the EU (Jamagne et al., 1995; Vossen et al., 1995; Jones et al., 2004; 2005).

(a) Water flux

q_{100} (m yr^{-1})

$q_{100} = -0.2849 + 0.8634P$; $R^2 = 0.97$

P (m yr^{-1})

(b) Water content

θ (m^3 m^{-3})

$\theta = 0.01479 + 0.9885\theta_{fc}$; $R^2 = 0.96$

θ_{fc} (m^3 m^{-3})
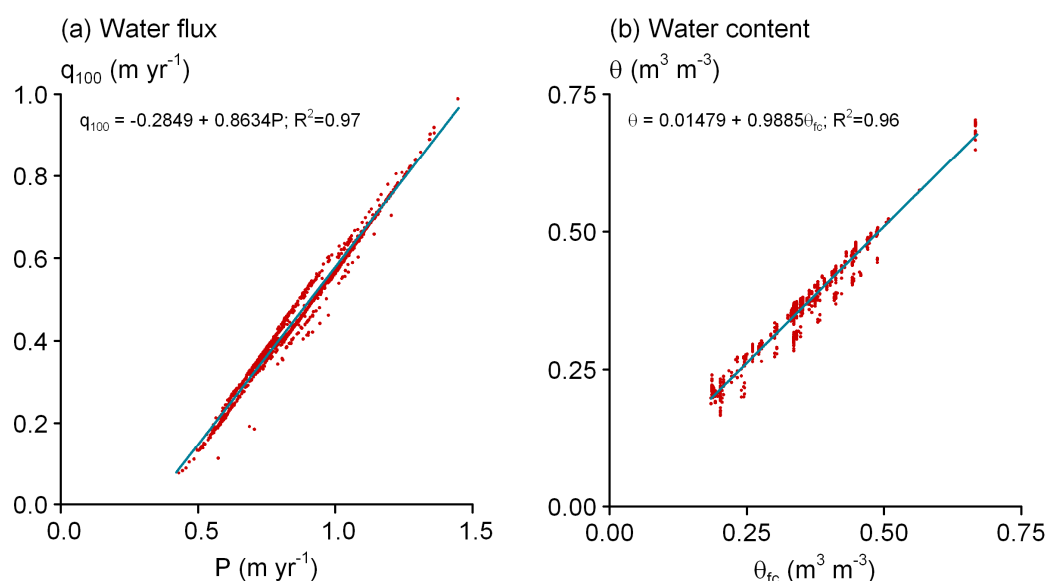
Figure A5-10. Relation between (a) mean annual precipitation (*P*) and the mean annual flux *q$_{100}$* at 100 cm depth and (b) relationship between water content at field capacity (θ*$_{fc}$*) and long-term average water content (θ). Both relationships were obtained from EuroPEARL simulations.

With the above described dataset, Tiktak et al. (2006) calculated leaching concentrations for the entire area of the EU-25 for Substances A and B. Maps of the leaching assessment are shown in Figure A5-11. To facilitate the interpretation of the predicted spatial patterns, maps of organic matter and precipitation surplus are presented as well. The predicted leaching concentrations generally increase with precipitation and decreases with increasing organic matter content (Figures A5-11c and A5-11d), which was expected. The leaching maps also show that the variability of the leaching concentration at short distances is considerable. This is caused by the strong sensitivity of pesticide leaching to the organic matter content, which shows a strong variability at short distances.
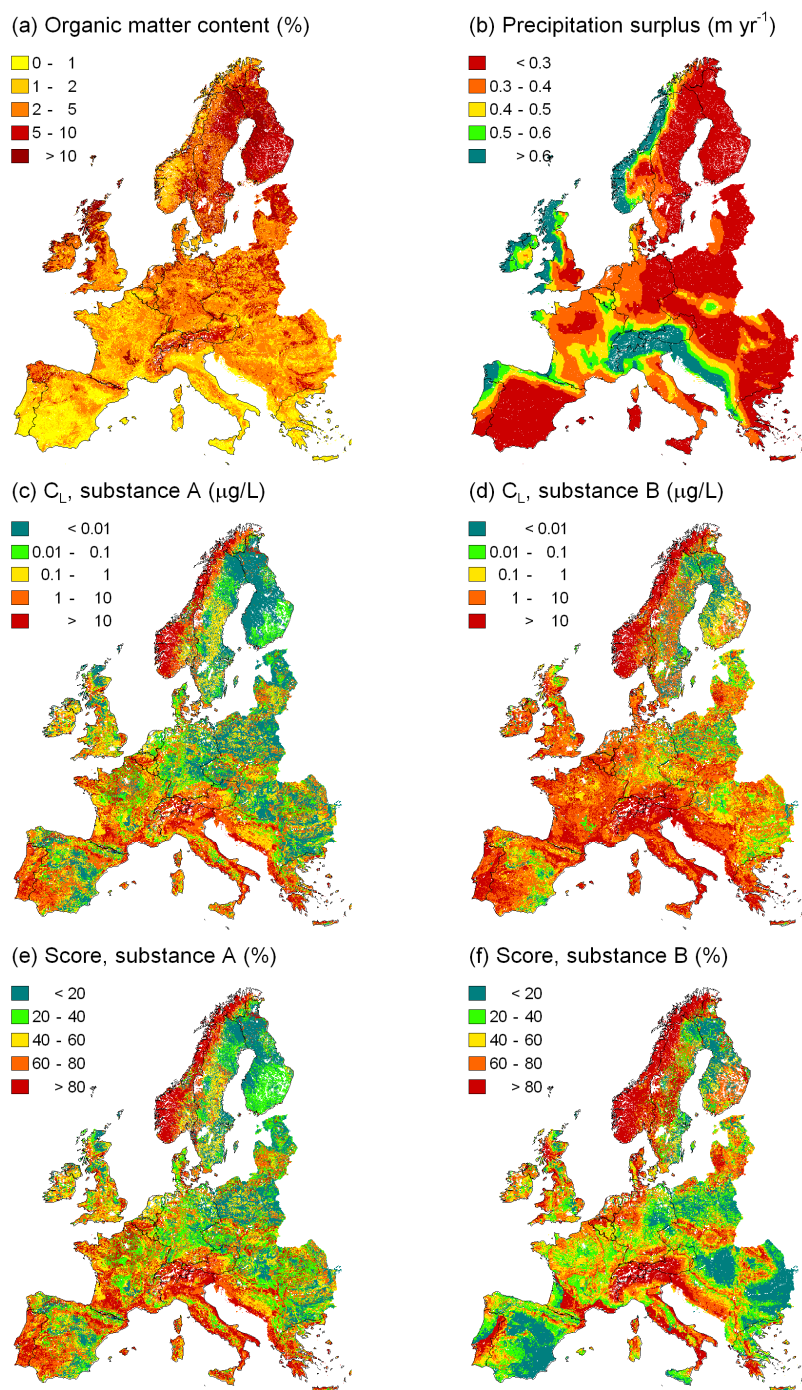
Figure A5-11. Results of the metamodel application at the entire EU-25. Leaching set autumn application was used. (a) Organic matter content of the upper meter of the soil profile; (b) annual mean precipitation surplus; (c) predicted leaching concentration for Substance A, (d) predicted leaching concentration for substance B; (e) normalized vulnerability score for Substance A; (f) normalized vulnerability score for Substance B.

The leaching maps also show that the predicted leaching concentrations in certain areas of southern Europe are relatively high. An explanation is found in the extremely low organic

matter contents in Mediterranean countries, which can be lower than 1% (Figure A5-11a). Also, in some regions in southern Europe (for example Galicia), precipitation is high.

The final product of the metamodel application is the ground water vulnerability map. In such a map, the leaching concentration is normalised: the grid-cell with the highest leaching scores 100%, while the grid-cell with the lowest leaching scores 0% (the normalised vulnerability score). As expected, the vulnerability score is generally high where precipitation surplus is high and organic matter is low (Figure A5-11ef). There are, however, important differences between the two substances. The vulnerability score of the very mobile Substance B shows much more resemblance with the precipitation surplus map than the vulnerability score of Substance A. The vulnerability score of Substance A is strongly correlated with the organic matter content map. These differences are in line with results obtained with the original model (Section A5.3), which suggests that the metamodel captures the main features with respect to the dependency of the leaching concentration on the various processes. This analysis further shows that pesticide properties must be included in ground water vulnerability assessments, particularly if the metamodel is used to derive use-specific scenarios (Section 7.2.5).

pH-dependent sorption and transformation

Van der Linden et al. (2001) developed a methodology to account for pH-dependent sorption and transformation. These procedures are included in the GeoPEARL model (Tiktak et al., 2003, Section 4.2). pH-dependent sorption and/or transformation can be easily incorporated into the metamodel. Equation A5-9 describes the X_2-term for ordinary behaving substances. When applying the metamodel, this equation should be replaced by the following expression for pH-dependent substances:

$$X_2 = \frac{\mu \rho f_{om} \dfrac{K_{om,ac} + Kom_{ba} \dfrac{M_{ba}}{M_{ac}} 10^{pH-pKa-\Delta pH}}{1 + \dfrac{M_{ba}}{M_{ac}} 10^{pH-pKa-\Delta pH}} L}{q} \tag{A5-17}$$

where $K_{om,ac}$ (m^3 kg^{-1}) is the coefficient for sorption on organic matter under acidic conditions, $K_{om,ba}$ (m^3 kg^{-1}) is the coefficient for sorption on organic matter under basic conditions, M (kg mol^{-1}) is molar mass, pKa is the negative logarithm of the dissociation constant, and ΔpH is a pH correction factor. See further the GeoPEARL manual (Tiktak et al., 2003) for details, particularly on using the pH-shift in an appropriate way.

Step 6: Selection of the target grid cell

The target grid cell(s) can be directly inferred from the normalized ground water vulnerability map. The following procedures should be followed:

- Frequency distributions should be created for the intended use area, using the crop area as a weighing factor (see the manual of GeoPEARL for procedures).
- All grid cells that meet the target vulnerability in the 80-85[th] vulnerability range should be selected as candidate scenarios. Notice that the use of a range is advocated instead of the exact 80[th] percentile, acknowledging that MetaPEARL is not a perfect metamodel of GeoPEARL.
- From the 80-85 percentile range, the grid cells with the highest crop area should be chosen as the final scenario (the dominant combination). This assures that representative unique combinations are chosen.

A5-5 Validation of the entire approach

As described in Sections 7.2.5 and A5.2, spatially-distributed models play an important role in the tiered assessment scheme. In Tier 2, simple spatially distributed models are used to derive use-specific scenarios (Section 7.2.5). The regulatory endpoint is calculated for this single scenario with a FOCUS leaching model. In Tier 3, spatially distributed are used to calculate the regulatory endpoint directly (Chapter 8).

As mentioned in Section 7.2.5, spatially-distributed models can be seen as the reference for simple leaching models, because the spatially distributed model uses the FOCUS leaching model directly. In this section, MetaPEARL is evaluated for using in developing scenarios for use in Tier 2b assessments. For this reason, MetaPEARL (model III) is applied to the Netherlands. This country was chosen, because a high quality soil, climate and crop data base is available, which covers the entire country. This makes it possible to calculate the FOCUS target percentile with both the original model (Tier 3 approach) and with use specific scenarios (Tier 2b approach). The validation consisted of the following elements:

- what is the correlation between the ground water vulnerability maps generated by the two methods?
- how do the results from a Tier 2b assessment compare to results of a Tier 3 assessment?

The validation was done for three pesticides (Table A5-3) and for 26 different use-specific scenarios. A secondary aim of the validation was to test if the general EU-metamodel parameterisation could be transferred to different data sets. This step is necessary in those

countries where insufficient soil information is available to build a local metamodel (see Section A5.2).

Comparison of the EU-Metamodel with a local metamodel

A metamodel of GeoPEARL for the Netherlands was built using the procedure described in Section A5.4. This metamodel parameterization was compared to the metamodel parameterization of the final EU-metamodel (model III). Because the Netherlands are in climatic zone TD (Table A5-2), this climatic zone was used for the final comparison. Results presented in Table A5-5 show that there are minor differences between the two metamodel parameterisations. The variance predicted by the Dutch metamodel (based on GeoPEARL_NL), however, is lower than the variance predicted by the EU-metamodel (based on EuroPEARL). In contrast to SPADE, the Dutch soil data base contains real soil profile descriptions (not estimated soil profiles). As a consequence, the data bases contain more extreme soil profiles than SPADE. Particularly clay on peat profiles cause additional scatter (see later text).

Table A5-5. Coefficients resulting from calibration of the metamodel to the two leaching sets.

Model†	Leaching set	Region‡	α_0 ***	α_1	α_2	α_3	R^2 *
Model III	Autumn	TD	5.30 (0.006)	0.16 (0.002)	0.46 (0.001)	NA	0.97
		NL	5.10 (0.014)	0.15 (0.003)	0.58 (0.001)	NA	0.89
Model III	Spring	TD	5.09 (0.007)	0.44 (0.003)	0.46 (0.001)	NA	0.95
		NL	4.85 (0.016)	0.43 (0.005)	0.38 (0.001)	NA	0.88

The rather good correspondence between the two metamodel parameterizations is confirmed when the two metamodels are used to predict ground water vulnerability in the Netherlands. If the EU-metamodel predictions are plotted as a function of the NL-metamodel predictions, a straight line with a 1:1 slope and few scatter results (Figure A5-12). The rather good correspondence between both metamodel parameterisation was a surprising result, because the two data sets were collected completely independent of each other (different soil and climate data bases were used to construct EuroPEARL and GeoPEARL). This exercise demonstrates that the EU-metamodel can be used to map ground water vulnerability in the

Netherlands. This exercise also indicates that the EU-metamodel can be used to map ground water vulnerability in those areas where building a local metamodel is not possible.
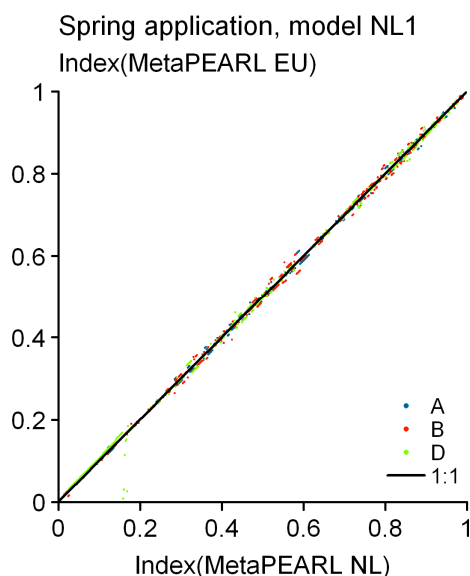
Figure A5-12. Ground water vulnerability calculated with the EU-Metamodel (climatic zone TD) as a function of the ground water vulnerability calculated with a metamodel based on the Dutch data base.

Comparison of the predicted spatial patterns of ground water vulnerability

Figure A5-13 shows the leaching concentration simulated with GeoPEARL as a function of the leaching concentration simulated with EU-Metamodel III. Figure A5-14 shows maps of the ground water vulnerability as predicted by the two models. Both models predict the highest ground water vulnerability in regions with extremely low organic matter contents and the lowest ground water vulnerability in regions with high organic matter contents. There are, however, also differences between the maps. Differences are most obvious in peat soils. In the Netherlands, many peat soils are covered with marine clay. In these soils, organic matter increases with depth. The metamodel cannot deal with differences in vertical depth distributions of organic matter, leading to a bias in the estimations. As a result of these differences, the correlation between the maps is lower than in the case of the EU-simulations (R^2 = 0.88 for substance A, 0.77 for substance B and 0.86 for substance D; see also Figure A5-13).
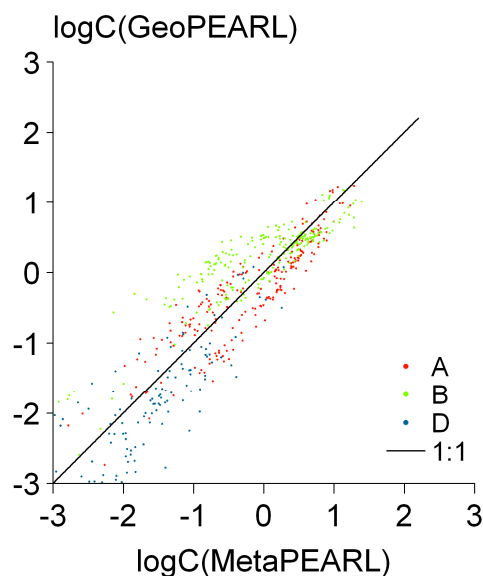
Figure A5-13. Leaching concentration (µg/L) simulated with GeoPEARL as a function of the leaching concentration (µg/L) simulated with MetaPEARL for the Netherlands.

Special case: pH-dependent sorption

As described before, GeoPEARL has options to simulate pH-dependent sorption. Both GeoPEARL and the EU-metamodel were used to predict the leaching pattern of the pH-dependent substance "NLD" (Tiktak et al., 2003). T his substance has a $K_{om,ac}$ of 500 L/kg, a $K_{om,ba}$ of 23 L/kg, a *p*Ka of 4.6 and a degradation half-life of 50 days. Results are shown in Figure A5-15. Notice that the leaching pattern of substance NLD is almost opposite to the leaching pattern of FOCUS substances A, B and D. Substance NLD is immobile in acidic sandy soils and mobile in near-neutral and basic soils. Notice that the classes 0-20 and 20-40 have been merged in the figure. The reason for this was that in the acidic sandy soils the leaching concentration was generally extremely low (less than 10^{-10} µg L^{-1}), which results in an almost random ranking. For registration purposes this range is not relevant.

GeoPEARL

Metamodel EU, TD

A

B

D

(-)
■   < 0.2
■   0.2 - 0.4
■   0.4 - 0.6
■   0.6 - 0.8
■   > 0.8
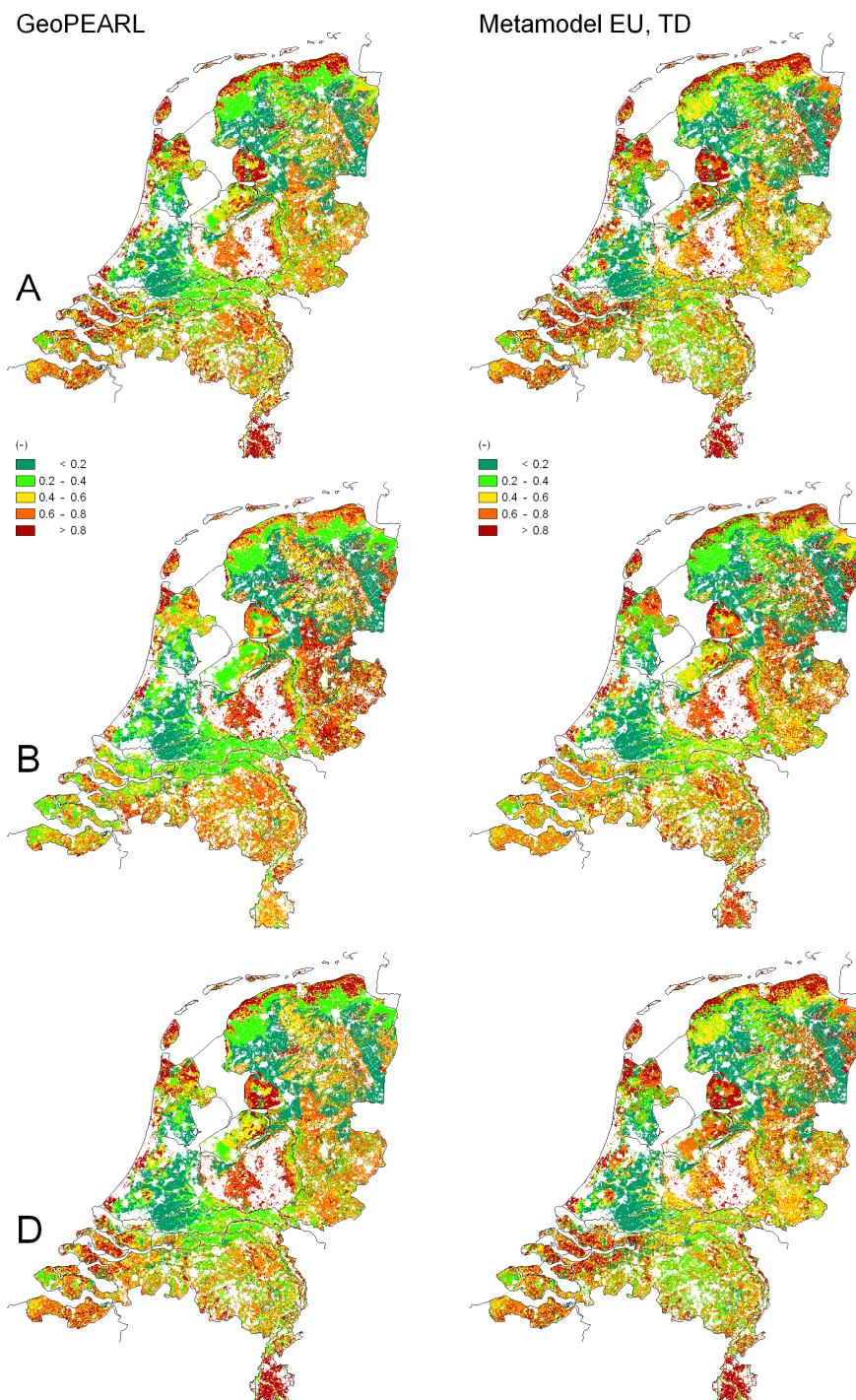
Figure A5-14. Predicted ground water vulnerability for FOCUS substances A, B and D. Right: calculated with MetaPEARL (EU model III). Left: calculated with GeoPEARL.
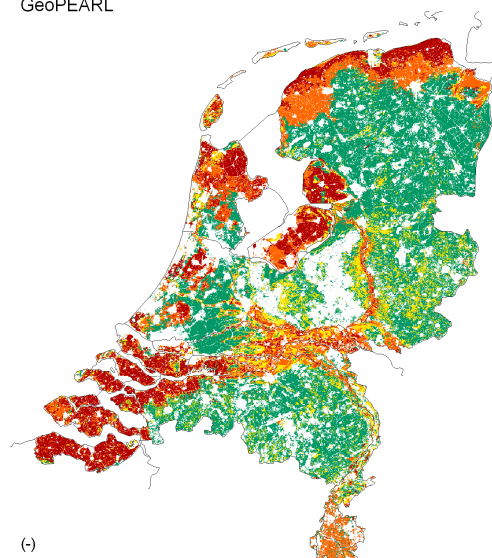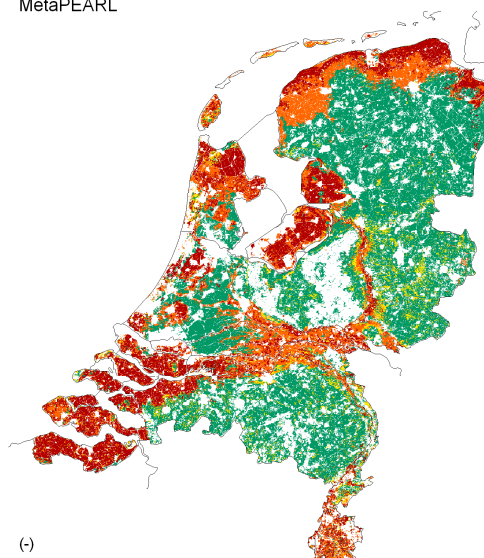
Figure A5-15. Predicted ground water vulnerability for a substance showing pH-dependent sorption (substance NLD). Right: calculated with MetaPEARL (EU model III). Left: calculated with GeoPEARL.

Comparison of regulatory endpoints

GeoPEARL is distributed with data on the distribution of 26 crops in the Netherlands (Kruijne et al., 2004). Figure A5-16 gives an example for two major crop types in the Netherlands, i.e. maize and potatoes. Maize is predominantly grown on acidic, sandy soils, while potatoes are predominantly grown on light-sandy clay soils. GeoPEARL was used to calculate the regulatory endpoint for EU-registration directly (see also Figure A5-1). Because a pesticide registration is often requested for a certain crop, the distribution of a crop can be seen as a substitute for the intended use area. The fact that data on crop distribution data are readily available in GeoPEARL, gives the opportunity to test the Tier 2b scenarios.

Distribution of major crops in the Netherlands

Maize

Potatoes

(% of arable land)
- < 5
- 5 - 10
- 10 - 15
- 15 - 20
- > 20

(% of arable land)
- < 5
- 5 - 10
- 10 - 15
- 15 - 20
- > 20
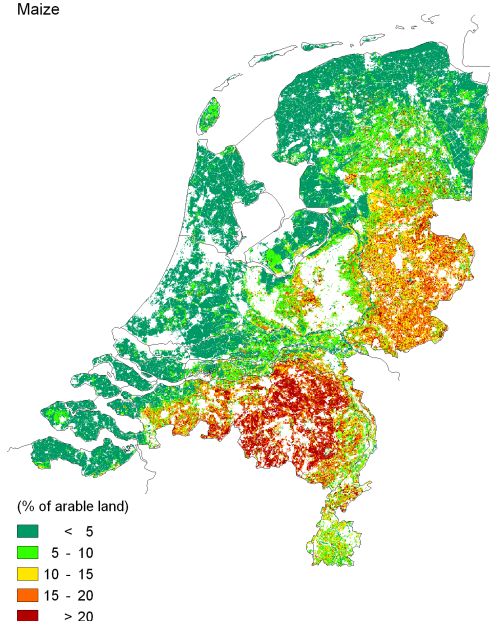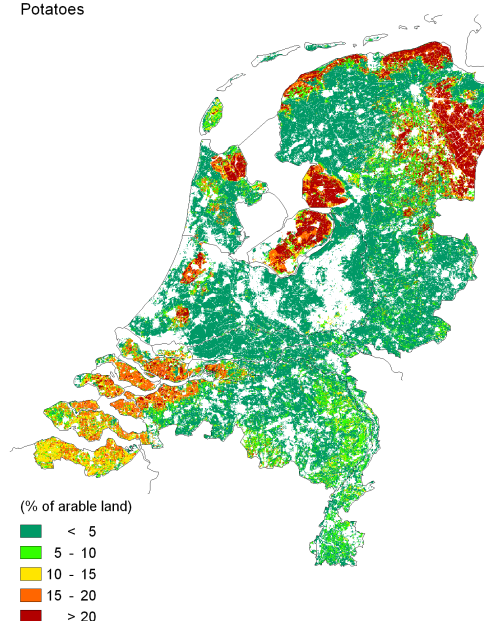
Figure A5-16. Distribution of two major crops (maize and potatoes) in the Netherlands. Crops are often seen as a substitute for the intended use area.

The following procedure was followed to select the target scenario from the leaching vulnerability map obtained with MetaPEARL (EU-model III):

- Frequency distributions were created for each individual crop, using the crop area as a weighing factor (see the manual of GeoPEARL for procedures).
- All unique combinations that meet the target vulnerability in the 80-85[th] vulnerability range were selected as candidate scenarios. Notice that we did not select the exact 80[th] percentile, acknowledging that MetaPEARL is not a perfect metamodel of GeoPEARL.
- From the 80-85 percentile range, the unique combination with the highest crop area was chosen as the final scenario (the dominant combination). This assures that rather 'normal' unique combinations are chosen.
- For this single scenario, FOCUS PEARL was run to calculate the final FOCUS target concentration.

Notice that in the Dutch case, the selection of scenarios is an easy (but not trivial) task, because the soils data have full spatial coverage. In many other areas of Europe (see for example the sugar beet case in Appendix 4 and Section 7.2.5), the selection of scenarios is a more complicated task. See Section 7.2.5 for possible procedures.

Figure A5-17 shows where the final scenarios are situated. The maize scenario is situated in the sandy part of the Netherlands, while the potatoes scenario is situated in a reclaimed polder area with light sandy clay soils. Apparently, the procedure of using dominant unique combinations promotes that the selected scenario is realistic. In all cases, however, the candidate scenarios should be checked for suitability (see Section 7.2.5 for details).
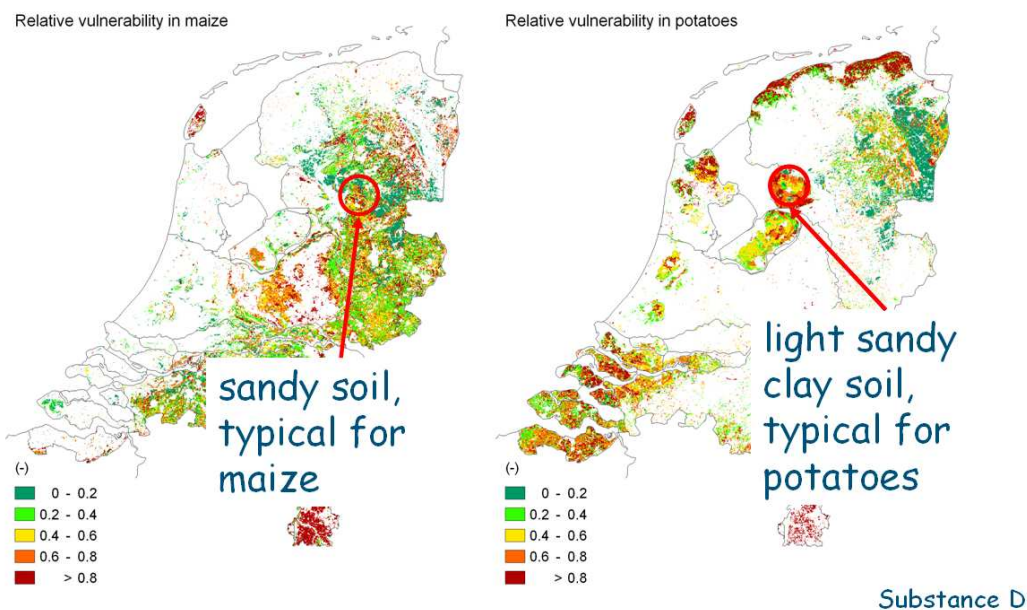
Figure A5-17. Specific ground water vulnerability for substance D and for two major crops. The position of the target tier 2b scenarios is shown as well.

For each of the 26 crops, the 80[th] percentile leaching concentration in the intended use area was also calculated directly with GeoPEARL (Tier 3 approach) for the national level of the Netherlands. In this way, we can directly compare the Tier 2b scenario with the Tier 3 approach. Figure A5-18 shows that the Tier 2b scenarios slightly overestimate the leached concentration, as compared to the Tier 3 scenarios. The overestimation results from the adopted procedure: the dominant plot from the 80-85[th] vulnerability range was selected. This guarantees that Tier 2b scenarios are slightly more conservative than calculations done with the Tier 3 approach, which is required in the tiered assessment scheme. The figures also show some scatter, particularly for substance B. This was expected, because MetaPEARL is not a perfect model of GeoPEARL. Also, ground water vulnerability maps for substance B showed the lowest correlation.

Comparison of scenarios selected with MetaPEARL and GeoPEARL
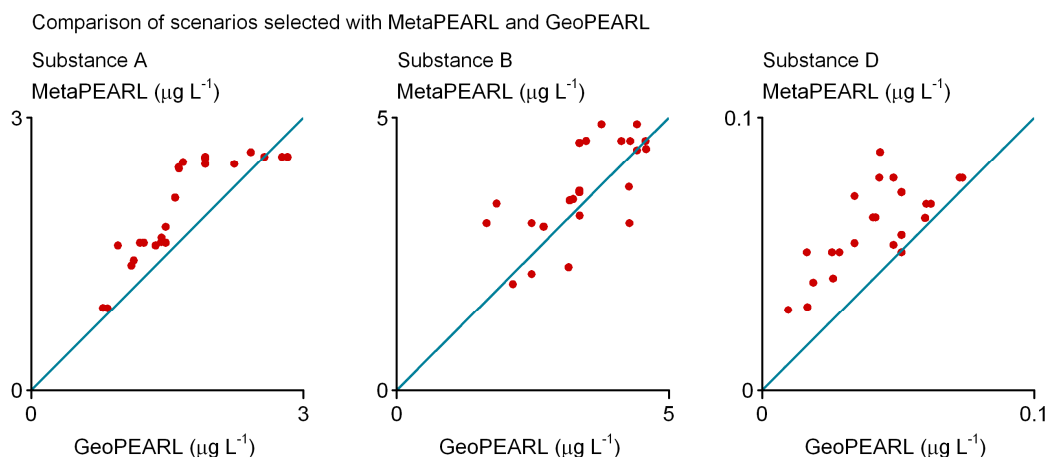
Figure A5-18. Tier 2b scenario calculations (selected ground water vulnerability maps predicted by MetaPEARL) as a function of Tier 3 calculations (simulated with GeoPEARL). The individual points are target concentrations for each of the 26 GeoPEARL crops.

A5-6. Sensitivity of MetaPEARL to some basic model inputs

MetaPEARL is a process based meta-model of the PEARL model developed to mimic PEARL and to cover the most important leaching processes of PEARL. If the processes are captured in a correct way, the sensitivity of MetaPEARL to changes in model inputs should be the same as the sensitivity of PEARL. To get a first impression of model sensitivities, we tested both FOCUS PEARL 2.2.2 and MetaPEARL for three FOCUS locations (Hamburg, Kremsmünster and Piacenza) and for four model inputs, i.e. the pesticide half-life ($DegT50$), the coefficient for sorption on organic matter (K_{om}), the mean annual precipitation (P) and the mean annual temperature (T). The sensitivities of other parameters (particularly bulk density and organic carbon content) were strongly correlated to the K_{om} and were therefore considered redundant for the evaluation. Changes of +/- 0, 2, 5, 10, 15, 20, 25% were made to the input parameters and the outputs (predicted concentrations) were recorded.

Regression analyses between the change of the input parameters and the change of the predicted concentrations were made and the slopes of the regressions were used as an indicator of the sensitivity. The Normalised Regression Coefficient (NRC) was calculated, which expresses the effect that a 1% change in the input parameter has an effect of x% change of the output (which is the concentration in the leachate). The NRC was calculated according to Equation A5-18:

$$NRC = SRC \cdot CV_y / CV_x \tag{A5-18}$$

where *NRC* is the normalised regression coefficient, *SRC* is the standardised regression coefficient, Cv_y is the coefficient of variation of % change of parameter *Y* and CV_x the coefficient of variation of % change of result *X*.

Parameter values for MetaPEARL were obtained from the FOCUS Tier 1 scenarios as follows:

- the long-term average precipitation and temperature were averaged over 20 FOCUS years (1907-1926). The water flux at 1 m depth was obtained from the long-term average precipitation using the transfer rule described in Figure A5-10;
- organic matter, bulk density and the soil water content at field capacity were obtained with an horizon weighted averaging procedure;
- K_{om} and *DegT50* were set to FOCUS default values.

Results

An example graphical illustration of the sensitivity analysis of MetaPEARL and FOCUS PEARL is given in Figure A5-19 for FOCUS substance D. The graph shows the change of the leaching concentration as a function of the change of the model inputs. The graph shows that the sensitivity of MetaPEARL is in rather good correspondence to the sensitivity of FOCUS PEARL for DegT50, K_{om} and temperature as long as the relative change of the input parameters is kept within 10%. MetaPEARL shows, however, a stronger sensitivity to the soil water flux at 100 cm depth than FOCUS PEARL.
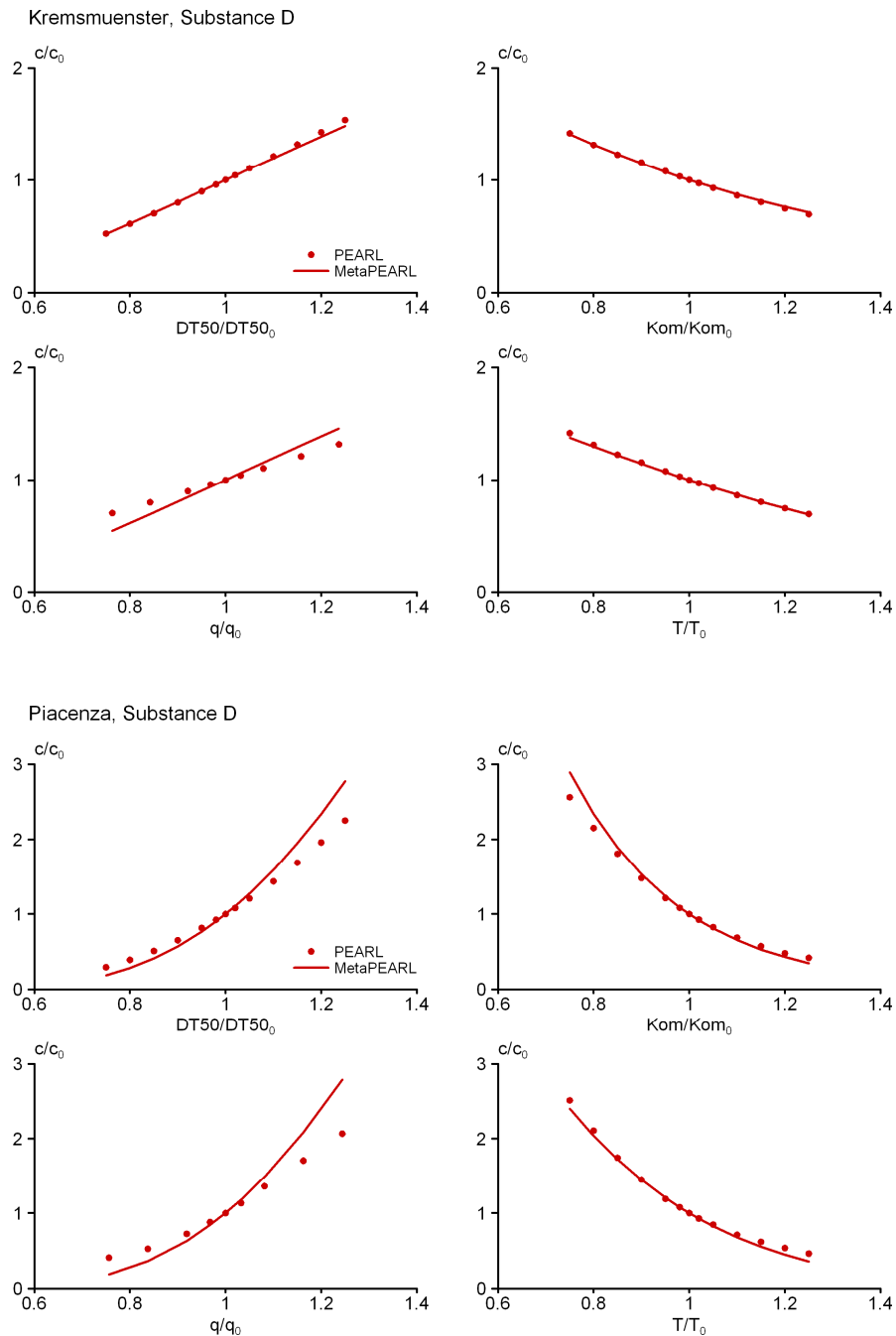
Figure A5-19. Sensitivity of the predicted leaching concentration in MetaPEARL to changes of different input parameters (example substance D at the Kremsmünster and Piacenza locations)

Table A5-6 shows a summary of the sensitivity analysis. The table shows the ratios of the normalised regression coefficients for MetaPEARL versus FOCUS PEARL. These ratios are considered as suitable measurements of the relative sensitivity of the two approaches. In the case of identical sensitivity, the ratio of the NRC's of MetaPEARL and FOCUS PEARL

should be near to unity. The table shows that the ratios are close to unity for $DegT50$, K_{om} and T, but deviate significantly for q.

Table A5-6. Average of the Normalised Regression Coefficients for the three FOCUS locations studied and for various model inputs and substances.

Substance	Parameter	NRC_{PEARL}	$NRC_{MetaPEARL}$	$NRC_{MetaPEARL}/NRC_{PEARL}$
A	$DegT50$	2.72	2.82	1.04
	K_{om}	-2.60	-2.59	1.00
	q	1.37	2.81	2.05
	T	-2.38	-2.33	0.98
B	$DegT50$	1.61	2.00	1.24
	K_{om}	-1.42	-1.30	0.91
	Q	1.02	2.00	1.95
	T	-1.38	-1.68	1.21
D	$DegT50$	4.04	5.15	1.27
	K_{om}	-4.54	-4.52	0.99
	Q	3.04	5.12	1.69
	T	-3.44	-3.76	1.09

The high sensitivity of MetaPEARL to the soil water flux is one of the reasons that a series of climatic zones was needed for metamodel calibration (see Section A5.4). As shown in Table A5-7, the coefficient of variation of precipitation and temperature within the climatic zones is low, particularly when compared to the other model inputs (K_{om}, $DegT50$ and organic matter). The homogeneousness of the climatic zones also explains why the spatial patterns of ground water vulnerability predicted by the metamodel are good (see Table A5-4). Apparently, the ranking is not affected as long as the climatic variation is kept within relatively small bounds. This also implies, however, that extrapolation of the metamodel to climatic zones that are not captured within the calibration dataset should be done with due care (see also the uncertainty section).

Table A5-7. Average of the input parameters in the EU-25 and in the four climatic zones described in Table A5-1. The table also shows the substance properties in the calibration dataset. Figures between brackets are the coefficient of variation of the input parameters.

	K_{om} (L/kg)	DegT50 (d)	f_{om} (kg/kg)	P (m/year)	Q (m/year)	T (^{o}c)
EU	49.88854 (88.9902)	100.1656 (58.1888)	0.034347 (247.242)	0.854514 (20.8209)	0.452432 (34.2270)	11.15401 (22.8115)
CD	49.07318 (89.7359)	100.867 (57.8006)	0.031101 (238.537)	0.713072 (11.263)	0.339283 (22.8181)	10.42166 (15.8137)
CW	50.71523 (88.3087)	99.50535 (58.4695)	0.043172 (251.734)	0.99064 (13.2601)	0.559165 (21.8099)	9.735488 (16.2062)
WD	49.72362 (88.986)	100.1463 (58.2878)	0.016361 (101.940)	0.646913 (12.0071)	0.266802 (27.3596)	15.40687 (9.67784)
WW	49.17781 (89.5015)	100.753 (58.0703)	0.028723 (132.238)	0.921471 (10.5147)	0.531426 (16.5543)	13.79488 (7.64002)

A5-7. Some remarks on uncertainty

A process-based metamodel of the leaching model EuroPEARL has been developed, which was successfully used to obtain quantitative leaching assessments for the entire area of the EU. Based on common knowledge of the leaching process, the behaviour of the model can be judged 'plausible'. Nevertheless, the model predictions are subject to a high degree of uncertainty. Errors result from the way how the system is conceived in the selected model and from the way how the model inputs and parameters have been generated (Loague and Corwin, 1996).

Model errors at the conceptual level arise when processes are inappropriately described by the model or when process descriptions are forced to be used in an application for which they were not initially intended. The metamodel inherits all the uncertainties associated with the original EuroPEARL model (Tiktak et al., 2004). A conceptual limitation of this model is for example related to the spatial-schematisation of the system. The properties of the environmental system vary extremely in space and time and this variability is now encoded by spatially distributing the environmental properties in a discrete way. Thereby, it is considered that the transport of pesticides from the land surface to the compliance depth passes through a set of 10X10 km^2 parallel soil columns. Variability of fate and transport processes at the surface and within these columns is completely ignored. Techniques for assessing the small-scale variability are still poorly developed and cannot be implemented at the European scale. An extreme example of this small scale variability is the ignorance of

preferential flow, a process for which consensus exists that is extremely important for correctly describing pesticide transport in soils (Flühler et al., 2001). Basic soil information for preferential flow models such as quantitative soil structure information (Rawls et al., 1996) is not yet available at the European scale, so whether a regional-scale version of preferential flow models will become available shortly remains questionable.

Input and parameter generation errors depend on the quality of the underlying data bases and the quality of the parameter generation techniques, such as the quality of the applied pedotransfer functions (Tiktak et al., 1999). For characterizing the spatial patterns of soil properties throughout Europe, the European Soil Map at the scale 1:1,000,000 was used in combination with the Soil Profile Analytical Database of Europe (Jamagne et al., 1995). The Soil Profile Database has serious limitations. The most serious limitations are that soil profile data is available for only 75% of the agricultural area of the EU-15, and that the soil profiles are not uniformly distributed across the continent. Jamagne et al. (1995) showed, however, that all major soil types are included. The metamodel was used to extend the simulations towards the entire EU. This can be done, as long as the metamodel is not applied beyond the range of values in the original data base. Analysis of the EuroPEARL data base revealed that only 6% of the total agricultural area of the EU-25 was outside the range of model inputs of the original model. The missing area is mainly in cold climates, where the mean annual temperature is below 5^{o}C. The effect of important processes for these regions, like snow accumulation and the effect of frost on water flow, may therefore be underestimated. Predictions for the Nordic and Baltic countries should, therefore, be treated with extra care. Another reason for being careful with metamodel extrapolation is the high sensitivity of the metamodel to the mean annual rainfall as compared to FOCUS PEARL (see Section A5.7).

The metamodel validation in this study pertains only to the comparison of the metamodel with the original model; no comparison with field-observations was made in this study. So far, leaching models have primarily been validated at the field-scale (e.g., Vanclooster et al., 2000; Trevisan et al., 2003) and very few studies, if any, have looked at the validity of the spatial leaching patterns simulated by spatially distributed leaching models. Analyzing the validity of the predicted spatial patterns needs detailed information on the occurrence of pesticides within ground water bodies. Unfortunately, high quality regional data sets that allow such an assessment are only available for some limited cases (e.g., Leterme et al., 2004; 2006; Tiktak et al., 2005). The EU-Groundwater Directive is expected to call for monitoring data on pesticide concentrations in the ground water, yet how data of such monitoring programs could be used to assess the validity of spatial predictions of pesticide leaching should be analysed.

When applying the metamodel, an additional error is added on top of the model error of the original model. Recently, a study started to quantify the error propagation in the chain EuroPEARL-metamodel (Van der Linden et al., 2006).

A5-8. General conclusions

<u>A tiered assessment scheme to spatially distributed modelling has been developed, which can be used to support both national and EU-registration.</u> In those cases where sufficient information is available, a process based, numerical leaching model can be used to calculate the regulatory endpoint directly. This is seen as a Tier 3 approach (Chapter 8). It can also be seen as a reference to other approaches, because it uses the original FOCUS leaching model directly. In those cases where data is insufficient, metamodels have been used to extend the simulations towards the entire intended use area. A single use-specific scenario is selected from the ground water vulnerability map obtained with this metamodel, and a FOCUS leaching model is run for this single scenario to get the regulatory endpoint (Tier 2b approach, Section 7.2.5). The approach can also be used to improve existing Tier 1 scenarios or to develop new Tier 1 scenarios (for national or EU-registration).

<u>Metamodels form the backbone of the approach reported in this appendix, because they guarantee consistency within the tiered assessment scheme.</u> We used a process-based metamodel of the recently developed European leaching model EuroPEARL. In contrast to earlier approaches, the metamodel is based on a large number of substances (56) and scenarios (1056). The metamodel explains more than 90% of the variation of the original model using only four independent spatially distributed parameters that are available from general soil and climate data bases. The calibrated metamodel was applied to generate maps of the leaching concentration in the European Union. Maps generated with the metamodel showed a striking similarity to maps obtained with EuroPEARL. The predicted leaching concentration generally increases with precipitation and decreases with increasing organic matter content. The short-distance variability of the leaching concentration due to organic matter overruled the north-south gradient caused by climatic differences, a leaching pattern that is also simulated by the original model. Quantitative performance indicators confirmed that the metamodel gives results comparable to the original model.

The entire approach was tested in the Netherlands, where sufficient soil data is available to parameterize a spatially distributed model with full coverage. The EU-Metamodel could be successfully applied to the Netherlands. This is an important result, because the data set for

the Netherlands was derived independently from the EU-data set. This is an indication that the metamodel can be used in countries where insufficient soil data is available to develop a spatially distributed leaching model, <u>so that the approach is applicable to the entire EU</u>. Results from Tier 2b scenarios with results from GeoPEARL (Tier 3 approach) showed a striking correspondence, indicating that the entire approach gives consistent predictions. <u>The Tier 2b scenarios were slightly more conservative than Tier 3 predictions, which indicates that the approach suites the general FOCUS tiered-assessment scheme</u> (earlier tiers must be more conservative than later tiers).

A5-9. Acknowledgements

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APPENDIX 6. EXAMPLE APPLICATION OF NON-EQUILIBRIUM SORPTION

As pointed out in Section 7.1.6, data from different kinds of experimental studies can be used to derive non-equilibrium parameters. Since the most common type of study is the (laboratory) aged sorption study the example used in this appendix is based on such a study. In this appendix, the example is worked with three different software tools (PEARLNEQ, ModelMaker, and MatLab) and two different object functions (see the example worked with MatLab for a discussion of the object functions).

Example Data Set

The following synthetic data set has been used to demonstrate the fitting procedure:

Compound. The test compound was assumed to have a K_{om} value of 100 L/kg, a DegT50 of approximately 130 days based on a DegT50eq of 90 days, f_{NE} of 0.7, and k_d of 0.012 (1/d).

Sorption Study. An aged sorption study was carried out using the basic design of a rate degradation study following OECD guideline 307. In addition to the total concentration (or residue mass per aliquot), a desorption step with an aqueous solution using another aliquot of each soil sample was carried out adding the same mass of $CaCl_2$-solution as the mass of the dry soil of the aliquot. The experimental conditions and assumptions used to generate the data set are shown in TableA6-1 and the generated measurements are provided in Table A6-2. Note that measurements in this table contain many more significant digits than is possible in reality. This was done to generate an ideal case for the optimisation procedure. The data were generated by forward modelling applying a randomly up to 5% uncertainty to the data.

372

Table A6-1. Experimental conditions of the laboratory aged sorption study and assumptions used to generate the data in Table A6-2.

Parameter	Unit	Value
Duration of study	[days]	148
Number of samples	[-]	8
OC	[%]	1.5
OM	[%]	2.586
DegT50eq	[days]	90
$K_{F,om,ads}$	[mL g^{-1}]	100
1/n	[-]	0.9
f_{NE}	[-]	0.7
k_d	(1/d)	0.012
Temperature	[°C]	20
Moisture	[%-grav]	14.92
Water added for desorption	[g]	Same mass as dry soil aliquot
Water-Soil ratio at desorption	[-]	1.1492 : 1
Applied concentration	[mg/kg]	1.0
Aliquot to measure total substance mass	[g]	0.5

Table A6-2. Generated measured values from the laboratory aged sorption study.

Sampling day	% of applied	Mass of substance per aliquot of 0.5 g [µg]	Concentration in suspension [mg/L]
0	98.12	0.490603	0.244624783
7	94.98	0.474897	0.214043703
14	88.76	0.443789	0.190843056
28	83.73	0.418639	0.155192812
61	67.55	0.337726	0.105507335
90	59.44	0.29718	0.079848608
120	51.09	0.255426	0.063528780
148	46.64	0.233218	0.054436049

PEARLNEQ

PEARLNEQ provided as a separate program package with the FOCUS_PEARL model, is a confined version of FOCUS-PEARL, where only those parameters essential for the simulation of the results of an aged sorption study can be varied. PEARLNEQ is coupled with the parameter estimation program PEST which runs PEARLNEQ by optimising the parameters to be estimated by minimising the sum of squared residues. The program package of PEARLNEQ includes the PEARLMK.EXE program that produces all necessary PEST files with the help of a make file. The program is DOS based and operates on command file or command line level. Boesten et al. (2007) provides a short description of PEARLNEQ.

In order to carry out the non-equilibrium parameter estimation procedure in PEARLNEQ, the make file of the PEARLNEQ package has to be compiled following the instructions in the PEARLNEQ manual. The make file of PEARLNEQ for the example case is listed in Table A6-3.

Table A6-3. PEARLNEQ Make file for the example case: "FOCUS_EXAMPLE.MKN".

```
 *------------------------------------------------------------------------------------
* STANDARD FILE for pearlmk version 4
* Program to fit the half-life, activation energy and parameters for long-term sorption
* kinetics of pesticides in soil
*
* This file is intended for use with the PEST program (Doherty et al., 1991).
* Please refer to the manual of PEARLNEQ
*
* (c) RIVM/MNP/Alterra 2003, 2005, 2006
*------------------------------------------------------------------------------------
* Model control
Yes             ScreenOutput
0.0             TimStart        (d)             Start time of experiment
148.0           TimEnd          (d)             End time of experiment
0.01            DelTim          (d)             Time step of output

* System characterization
0.5             MasIni          (ug)            Initial guess of initial mass
0.5             MasSol          (g)             Mass of soil in incubation jar
0.0746          VolLiqSol       (mL)            Volume of liquid in the moist soil
0.5             VolLiqAdd       (mL)            Volume of liquid ADDED
0.02586         CntOm           (kg.kg-1)       Organic matter content

* Sorption parameter
1.0             ConLiqRef       (mg.L-1)        Reference liquid content
0.9             ExpFre          (-)             Freundlich exponent
100             KomEql          (L.kg-1)        Coefficient for equilibrium sorption
0.5             FacSorNeqEql    (-)             Initial guess of ration KfNeq/KfEql
0.01            CofRatDes       (d-1)           Initial guess of desorption rate constant

* Transformation parameters
100.00          DT50Ref         (d)             Initial guess of half-life at ref.
conditions
20.0            TemRefTra       (C)             Reference temperature
54.0            MolEntTra       (kJ.mol-1)      Initial guess of molar activation energy

* Temperature at which the incubation experiments are being carried out
table Tem (C)
1  20.0
end_table

* Provide the measured concentrations
* Tim  Tem  Mas       Con
* (d)  (C)  (ug)      (ug/L)
table Observations
0     20   0.490602654   0.244624783     OBS
7     20   0.474897155   0.214043703     OBS
14    20   0.443788719   0.190843056     OBS
28    20   0.418638994   0.155192812     OBS
61    20   0.337726508   0.105507335     OBS
90    20   0.297180245   0.079848608     OBS
120   20   0.255426161   0.063528780     OBS
148   20   0.233219313   0.054436049     OBS
end_table

* Procedure of weighing of data
equal           Opt_weights
```

Running the PEARLMK program produces a series of files that are necessary to run the PEST optimisation. The key file is the PEST steering file with the extension "*.PST". The respective steering file of the example is shown in Table A6-4.

Table A6-4. PEARLNEQ FOCUS_EXAMPLE.PST file for the example case using weights proportional to the inverse of the measured value. The observations o1, o3, o5 etc are masses of the substance and the observations o2, o4, o6 etc are concentrations in the liquid phase.

```
pcf
* control data
restart
   4   16    4 0
1 1 single point
5.0 2.0 0.4 0.03 10
3.0 3.0 1.0e-3
0.1
30 0.01 3 3 0.01 3
1 1 1
* group definitions and derivative data
FSNE    relative 0.01  0.0   switch  2.0 parabolic
CRD     relative 0.01  0.0   switch  2.0 parabolic
DT50    relative 0.01  0.0   switch  2.0 parabolic
MASINI relative 0.01   0.0   switch  2.0 parabolic
* parameter data
FSNE    none relative       0.5000  0.1    10.0 FSNE   1.00  0.00
CRD     none relative       0.0100  1.e-3  0.5  CRD    1.00  0.00
DT50    none relative     100.0000  1.0  500.0  DT50   1.00  0.00
MASINI none relative        0.5000  0.0 1000.0  MASINI 1.00  0.00
* observation data
 o1             0.49060265                 2.038
 o2             0.24462478                 4.088
 o3             0.47489716                 2.106
 o4             0.21404370                 4.672
 o5             0.44378872                 2.253
 o6             0.19084306                 5.240
 o7             0.41863899                 2.389
 o8             0.15519281                 6.444
 o9             0.33772651                 2.961
o10             0.10550733                 9.478
o11             0.29718025                 3.365
o12             0.07984861                12.524
o13             0.25542616                 3.915
o14             0.06352878                15.741
o15             0.23321931                 4.288
o16             0.05443605                18.370
* model command line
c:\Models\FOCUSPEARL_3_3_3\PEARL_NEQ\bin\PearlNeq Focus_example
* model input/output
Focus_example.tpl   Focus_example.neq
Focus_example.ins   Focus_example.out
```

PEARLNEQ offers two options for weighing of data: unweighted (thus giving equal weight to all measurements)and a weight proportional to the inverse of each measured value (thus giving equal weight to all measurements). In the example case the magnitude of the total substance masses and the liquid concentration of the suspension is within the same order of

magnitude (see column of observation values o1 to o16 in Table A6-4) and therefore equal weighting of all data points might be justified. So both types of weighing were used and the results were compared.

After PEST is started (command file or command line), PEST runs the PEARLNEQ model, which produces an output file as shown in Table A6-5. The results of the output file are then compared to the measured data by the PEST program and the parameters are optimised until the sum of squared residues is minimised. Running the PEST optimisation for the example case yields the results as shown in Table A6-6. This table shows that the two different weighing methods produced parameter estimates that were very close to each other. However, the 95% confidence limit intervals for the equal weights are considerable wider than those for the weights proportional to the inverse of the measured value.

Table A6-5. Output file of PEARLNEQ - FOCUS_EXAMPLE.OUT (assuming equal weights)

```
* --------------------------------------------------------------------------------
* Results from PEARLNEQ (c) MNP/RIVM/Alterra
* PEARLNEQ version 4
* PEARLNEQ created on                          : 27-Jul-2007
*
* Run ID                                       : Focus_example
* Input file generated on                      : 27-07-2007
* --------------------------------------------------------------------------------
*

  ------------------------------------------------------------
* System properties
* Mass of dry soil (g)                 :     0.5000
* Volume of water in moist soil (mL)   :     0.0746
* Volume of water added (mL)           :     0.5000
* Initial mass of pesticide (ug)       :     0.4962
* Reference concentration (ug.mL-1)    :     1.0000
* Equilibrium sorption coeff (mL.g-1)  :     2.5860
* Non-equili. sorption coeff (mL.g-1)  :     1.7602
* Freundlich exponent (-)              :     0.9000
* Desorption rate coefficient (d-1)    :     0.0125
* Half-life transformation (d)         :    91.4001
* Reference temperature (K)            :   293.1500
  ------------------------------------------------------------

*  Temp   Time            Mas           ConPor            XNeq           ConSus
*   (C)   (d)             (ug)         (ug.mL-1)        (ug.g-1)        (ug.mL-1)
    20.0   0.0       0.49615232       0.32623459      0.00000000       0.24017080
    20.0   1.0       0.49241869       0.32064264      0.00793694       0.23615477
    20.0   2.0       0.48874284       0.31518177      0.01565288       0.23223111
    20.0   3.0       0.48512350       0.30984864      0.02315324       0.22839751
    20.0   4.0       0.48155945       0.30464000      0.03044329       0.22465173
    20.0   5.0       0.47804947       0.29955269      0.03752818       0.22099159
    20.0   6.0       0.47459240       0.29458363      0.04441294       0.21741495
    20.0   7.0       0.47118710       0.28972980      0.05110248       0.21391973
    20.0   8.0       0.46783243       0.28498830      0.05760159       0.21050392
    20.0   9.0       0.46452731       0.28035626      0.06391494       0.20716555
    20.0  10.0       0.46127067       0.27583092      0.07004709       0.20390268
    20.0  11.0       0.45806147       0.27140957      0.07600250       0.20071345
    20.0  12.0       0.45489868       0.26708594      0.08178552       0.19759603
    20.0  13.0       0.45178133       0.26286840      0.08740038       0.19454864
    20.0  14.0       0.44870842       0.25874106      0.09285123       0.19156955
    20.0  15.0       0.44567903       0.25471007      0.09814205       0.18865708
```

Table A6-6. Results of the example case as found in FOCUS_EXAMPLE.REC.

Part A: All weights equal

```
                        OPTIMISATION RESULTS


Parameters ----->

Parameter         Estimated          95% percent confidence limits
                  value              lower limit       upper limit
 fsne             0.680674           0.536317          0.825031
 crd              1.252999E-02       7.691359E-03      1.736862E-02
 dt50              91.4001            87.2686            95.5316
 masini           0.496152           0.490922          0.501383
```

Part B: weights proportional to inverse of measured value

```
                        OPTIMISATION RESULTS


Parameters ----->

Parameter         Estimated          95% percent confidence limits
                  value              lower limit       upper limit
 fsne             0.683095           0.638053          0.728136
 crd              1.258243E-02       1.081117E-02      1.435369E-02
 dt50              90.8443            88.0157            93.6729
 masini           0.497186           0.491482          0.502891
```

ModelMaker 3.0

ModelMaker is one of the tools that are recommended for parameter fitting within the
framework of FOCUS kinetics (a more detailed description can be found in FOCUS, 2006).
Gurney and Hayes (2007) describes an implementation the non-equilibrium sorption
approach according to Boesten et al. (1989) and Leistra et al. (2001). This approach is
outlined in Figure A6-1. By enabling of the function "least squares" all data are equally
weighted.
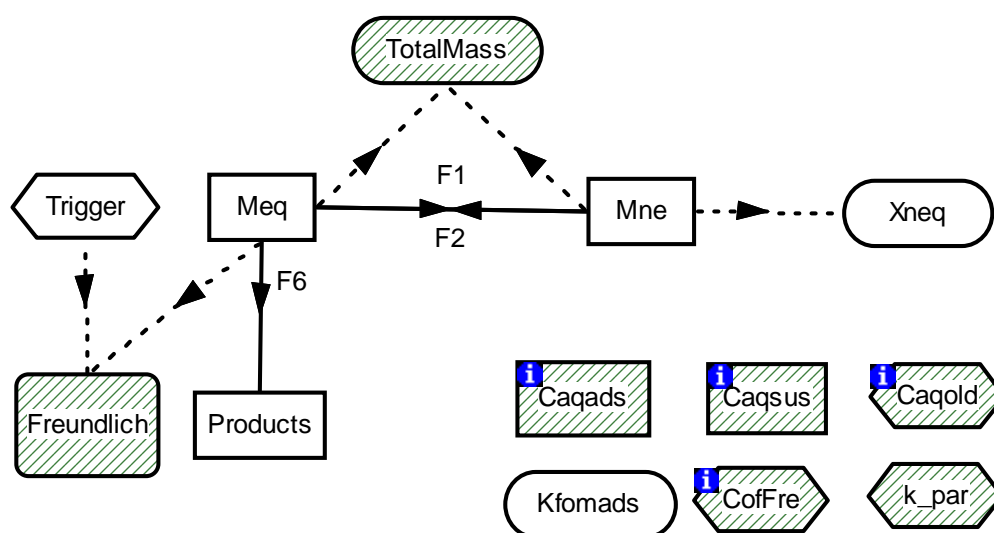
Figure A6-1. Implementation of non-equilibrium sorption in ModelMaker 3.0.

The implementation of the non-equilibrium sorption in ModelMaker according to Gurney and Hayes (2007) uses the same or similar nomenclature as in PEARLNEQ. The two data sets for the example, the total mass in [μg] and the liquid concentration in the suspension in [μg/mL], are shown in Figure A6-2.
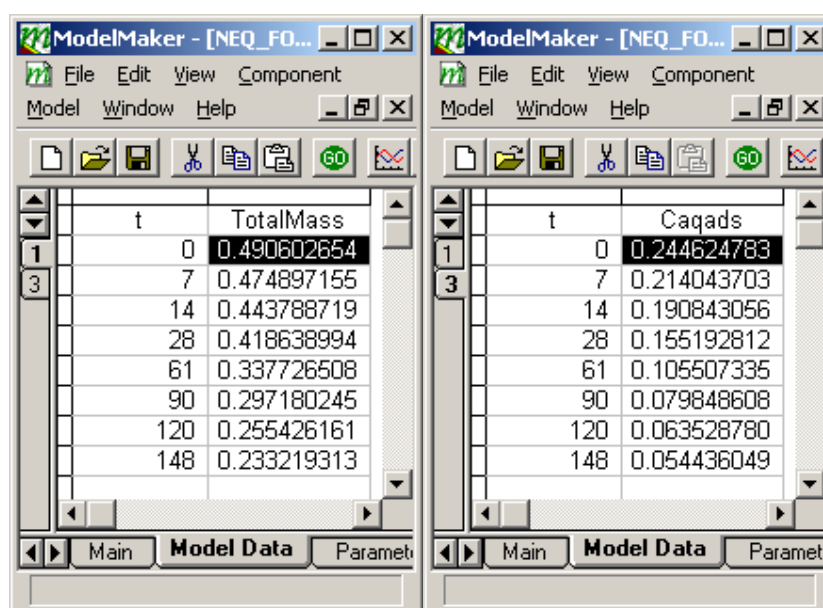
Figure A6-2. Model data for the fit of the example case with ModelMaker.

Figure A6-3 provides the values of the initial and the fixed parameters and Figures A6-4 and A6-5 show the optimisation configuration.

Figure A6-3. Initial or fixed set of parameters for the ModelMaker 3.0 fit of the example case.
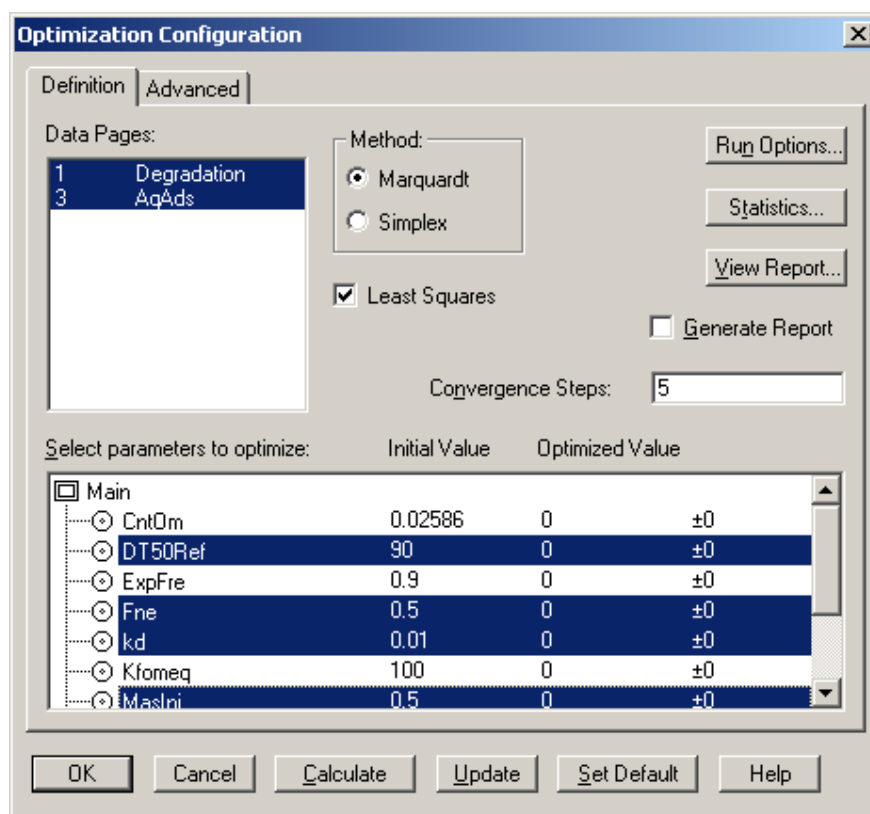
Figure A6-4. Setup of the optimisation configuration definition in ModelMaker 3.0 fit for the example
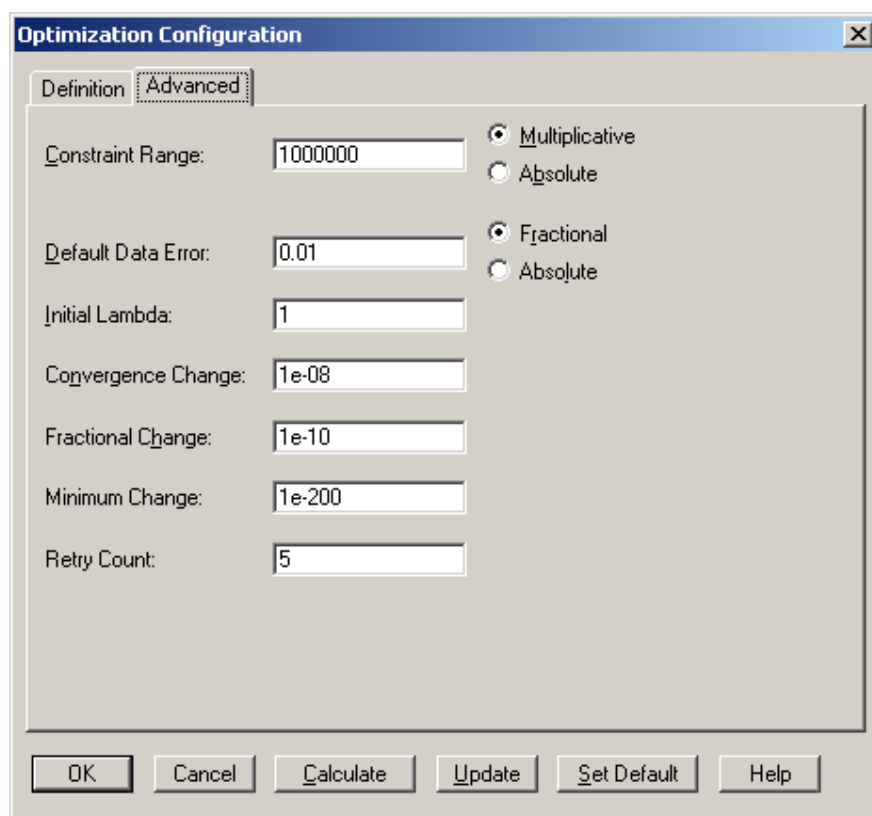
Figure A6-5. Setup of the advanced optimisation configuration in ModelMaker 3.0 fit for the example

The resulting estimates for the non-equilibrium sorption parameters as well as their standard deviations using the optimisation approach of ModelMaker 3.0 are shown in Figure A6-6. Graphical representations are shown in Figures A6-7 and A6-8.
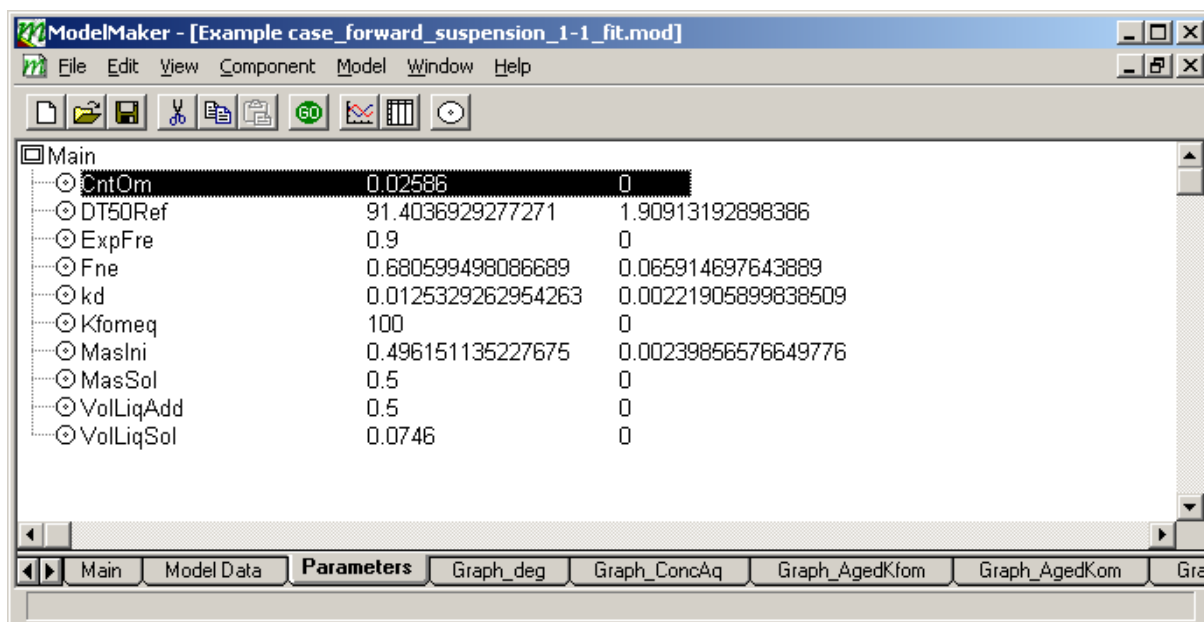
Figure A6-6. Results of the parameter estimation process with ModelMaker 3.0.
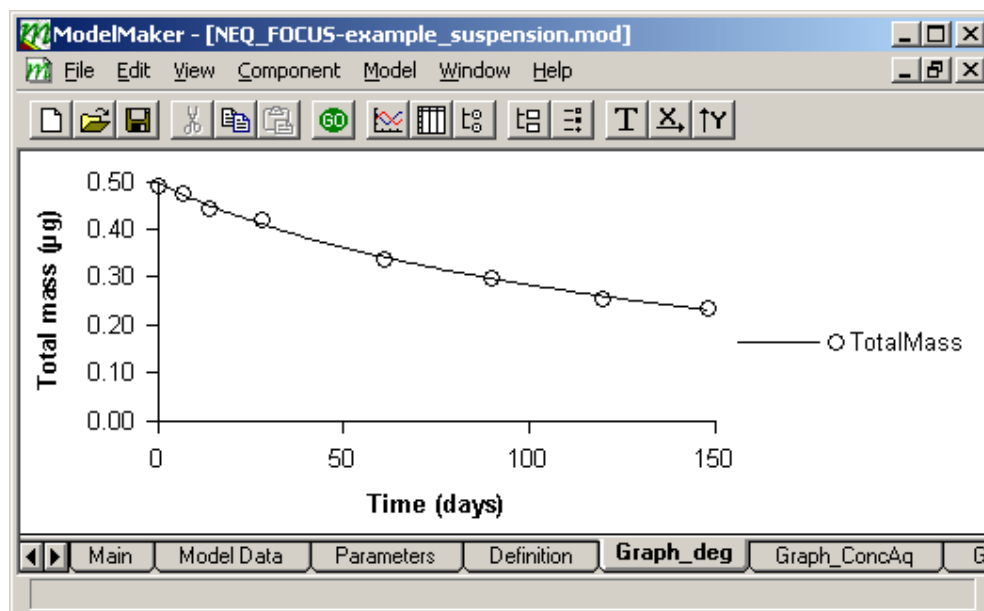
Figure A6-7. Results of the fit of the total substance mass with ModelMaker 3.0.
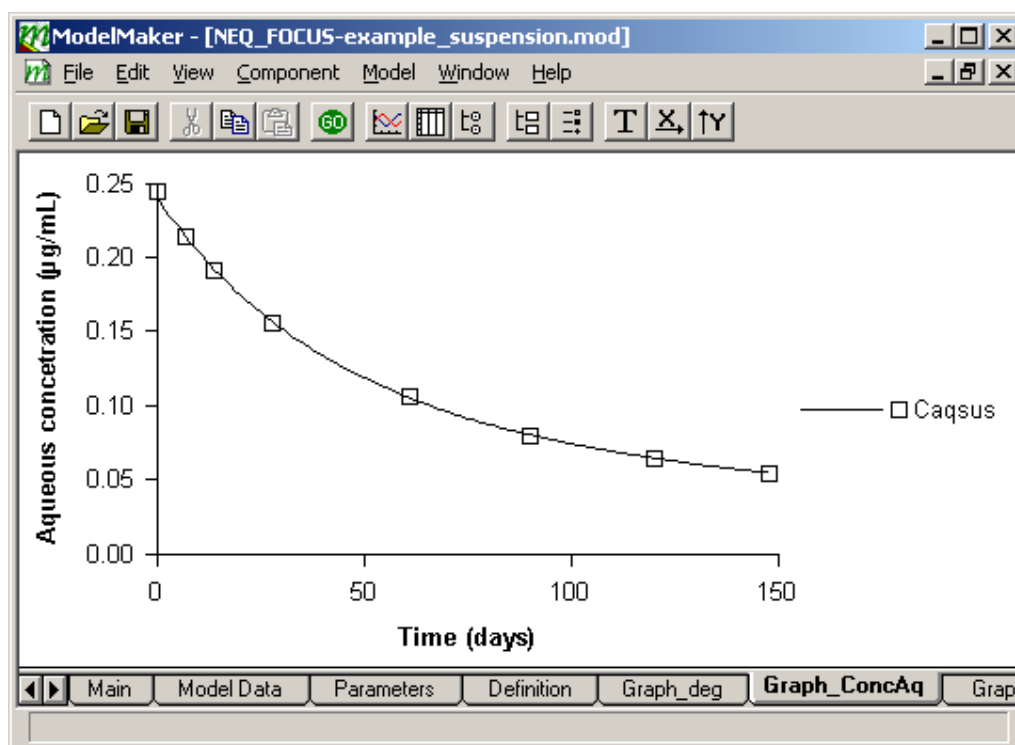
Figure A6-8. Results of the fit of the concentration in the liquid phase of the suspension with ModelMaker 3.0.

S_{eq} - S_{neq} approach, using MatLab

As described before, there are two main alternative possibilities to set up the object function to determine parameters for the kinetic sorption model. One is to let the model fit the concentration in the supernatant of the desorption solution $C_{l\,des}$ and the total mass M_t (M_t - $C_{l\,des}$ approach, as described previously in the examples with the tools PEARLNEQ and ModelMaker). Another approach is to calculate back the concentrations (C_l, S_{eq}, S_{neq}) in the soil before the $CaCl_2$ desorption and performing the fit on these concentrations (S_{eq} - S_{neq} approach). Both approaches should in principle give the same results.

Kley and Hammel (2008) describe the implementation of the non-equilibrium sorption approach according to Boesten et al. (Boesten et al., 1989) and Leistra et al. (2001) using equilibrium (S_{eq} or C_l) and non-equilibrium sorbed concentrations (S_{neq}) of the originally unsaturated soil sample before any dilution as fitting variables. The approach can be implemented in several mathematical tools, e.g. MatLab (MatLab, 2007), ModelMaker (ModelMaker, 2000), ACSL (ACSL, 1996) or others, which are considered equivalent, when implemented accordingly. The following example evaluations were investigated using MatLab.

Pre-processing of the Data

In PEARLNEQ and ModelMaker (as implemented in the example in this appendix) the concentrations in the suspension can be directly fitted, since the models internally recalculate the concentrations in the unsaturated soil solution.

If the fit should be done to S_{eq} and S_{neq}, which are concentrations in the originally unsaturated / undiluted system, pre-processing is necessary to recalculate experimental measures to the original concentrations in the unsaturated soil, i.e. the pore water C_l and the amounts sorbed to equilibrium S_{eq} and non-equilibrium sites S_{neq}. These variables are needed in each model (also PEARL and ModelMaker as used here); the difference is if the comparison between measurements and simulation is made for diluted concentrations ($C_{l\,des}$, M_t) or for the unsaturated system concentrations (C_l, S_{eq} and S_{neq}).

Pre-processing can be done with the same software as the final fit or in a spreadsheet calculation. The following example evaluations were done using Microsoft Excel and MatLab. The pre-processing to obtain concentrations compatible with PEARL is described in the following (for details see Kley and Hammel, 2008).

Step 1. Calculation of the total mass in the equilibrium phase

The total mass in the equilibrium phase M_{EQ} can be calculated by multiplying the concentration in the liquid phase $C_{l\,des}$ with the volume of the liquid phase $V_{w\,des}$ (soil pore water and $CaCl_2$ solution added for desorption) and adding the product of the soil dry mass M_0 and the equilibrium phase concentration $S_{eq\,des}$ in the soil:

$$M_{EQ} = C_{l\,des} \bullet V_{w\,des} + S_{eq\,des} \bullet M_0 \tag{A6-1}$$

$S_{eq\,des}$ can be calculated using the Freundlich equation:

$$S_{eq\,des} = K_{F,eq} \bullet C_{l\,des}{}^{1/n} \tag{A6-2}$$

where $C_{l\,des}$ and $S_{eq\,des}$ refer to the conditions after $CaCl_2$ desorption or dilution. For the test data $K_{F,eq} =$ is 2.586 L kg^{-1} and the Freundlich exponent ($1/n$) is 0.9. The assumed dry mass of the soil aliquot is $M_0 = 0.5$ g and therefore the added mass of water also 0.5 mL. The amount of the soil pore water is 0.0746 mL resulting in a total liquid phase volume of $V_{w\,des} =$ 0.5746 mL. Table A6-7 shows the calculation of the total equilibrium phase mass for the example data set.

Table A6-7. Calculation of total mass in the equilibrium phase of the suspension/supernatant solution system.

Sampling day	Measured concentration in liquid phase $C_{l\ des}$ [mg/L]	Concentration in equilibrium soil phase $S_{eq\ des}$ [mg/kg]	Mass in liquid phase $C_{l\ des} \bullet V_{w\ des}$ [µg]	Mass in equilibrium soil phase $S_{eq\ des} \bullet M_0$ [µg]	Total mass in equilibrium phase M_{EQ} [µg]
0	0.24462	0.72825	0.14056	0.36412	0.50469
7	0.21404	0.64577	0.12299	0.32289	0.44588
14	0.19084	0.58242	0.10966	0.29121	0.40087
28	0.15519	0.48352	0.08917	0.24176	0.33093
61	0.10551	0.34165	0.06062	0.17083	0.23145
90	0.07985	0.26587	0.04588	0.13293	0.17882
120	0.06353	0.21642	0.03650	0.10821	0.14471
148	0.05444	0.18833	0.03128	0.09417	0.12545

Step 2. Calculation of the equilibrium phase components of unsaturated soil

Now the total mass in the equilibrium sorption phase has to be distributed to the liquid and solid phase of the original moist or unsaturated soil, before the $CaCl_2$ desorption. For this purpose, the total equilibrium phase mass immediately before and after $CaCl_2$ desorption can be assumed to be equal, because the transfer from or to the non-equilibrium sites takes time.

Before desorption the liquid phase is represented by the pore water V_w, which is 0.0746 mL per aliquot M_0 of 0.5 g dry soil. Thus the total mass in equilibrium phase can also be written as:

$$M_{EQ} = C_l \bullet V_w + S_{eq} \bullet M_0 \tag{A6-3}$$

S_{eq} can be calculated again using the Freundlich equation:

$$S_{eq} = K_{F,eq} \bullet C_l^{1/n} \tag{A6-4}$$

leading to:

$$M_{EQ} = C_l \bullet V_w + K_{F,eq} \bullet C_l^{1/n} \bullet M_0 \tag{A6-5}$$

where all variables are known except C_l. Due to the non-linearity of the Freundlich equation C_l cannot be calculated directly but has to be solved numerically using for example EXCEL spreadsheets in combination with SOLVER or GOAL-SEEK function, which is described in Table A6-8. In the first line of Table A6-8 the column numbers are given, in the second the corresponding inputs for the EXCEL cells which are either numbers (e.g. column (6)) or functions. The SOLVER algorithm requires basically three inputs: i) the cells to be changed

(column (2)), ii) the goal cells (column (8)) which are compared to iii) the goal value, which in this case is 0.

Running SOLVER produces a numerical solution of C_l (column (2)), which is the base for further calculations in this spreadsheet. For column (2) start values are needed, which can be set to $C_{l\,des}$ (Table A6-7).

Table A6-8. Calculation of the equilibrium phase soil and pore water concentration for the unsaturated soil before desorption.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	changed by EXCEL SOLVER	$= K_{F,eq} \cdot (2)^{1/n}$	$= (2) \cdot V_w$	$= (3) \cdot M_0$	input	$= (4) + (5)$	$((6) - (7))^2$ goal cell for EXCEL SOLVER
Sampling day	Concentration		Mass [µg]				Squared residuals
	Pore water C_l [mg/L]	Equilibrium phase soil S_{eq} [mg/kg]	Pore water	Equilibrium phase soil	Reference total equilibrium phase M_{EQ}	Calculated total equilibrium phase	$[µg]^2$
0	0.33244	0.95977	0.02480	0.47989	0.504685	0.504685	0.00000
7	0.28990	0.84850	0.02163	0.42425	0.445876	0.445877	0.00000
14	0.25774	0.76328	0.01923	0.38164	0.400869	0.400869	0.00000
28	0.20852	0.63075	0.01556	0.31538	0.330933	0.330933	0.00000
61	0.14044	0.44195	0.01048	0.22097	0.231450	0.231450	0.00000
90	0.10559	0.34188	0.00788	0.17094	0.178816	0.178816	0.00000
120	0.08356	0.27696	0.00623	0.13848	0.144715	0.144715	0.00000
148	0.07135	0.24025	0.00532	0.12012	0.125445	0.125445	0.00000
sum							0.00000

As expected the mass in pore water is much lower before desorption and the mass in the equilibrium phase much higher. Nevertheless liquid concentrations are higher before desorption due to the simultaneous change of the water:soil ratio (water volume is increased by a factor of approximately 8).

Step 3. Calculation of the mass in the non-equilibrium phase
The final step is the calculation of the mass M_{neq} and concentration S_{neq} in the non-equilibrium phase, as the difference between the total mass M_t and the mass in the equilibrium phases M_{eq} (solved and sorbed).

$$M_{neq} = M_t - M_{eq} \qquad\qquad\qquad (A6-6)$$

$$S_{neq} = M_{neq} / M_0 \qquad\qquad\qquad (A6-7)$$

For the example data set the results are shown in Table A6-9. At day zero $M_{neq} = 0$ by definition and thus corresponding values are not shown in Table A6-9. Values for C_l and S_{eq} were taken from Table A6-8.

Table A6-9. Calculation of concentration in the non-equilibrium phase of the unsaturated soil.

Sampling day	Conc. pore water C_l [mg/L]	Conc. equilibrium soil phase S_{eq} [mg/kg]	Total mass equilibrium phase M_{EQ} [µg]	Total mass measured M_t [µg]	Mass non-equilib. phase M_{neq} [µg]	Conc. non-equilib. phase S_{neq} [mg/kg]
7	0.290	0.849	0.446	0.475	0.029	0.058
14	0.258	0.763	0.401	0.444	0.043	0.086
28	0.209	0.631	0.331	0.419	0.088	0.175
61	0.140	0.442	0.231	0.338	0.106	0.213
90	0.106	0.342	0.179	0.297	0.118	0.237
120	0.084	0.277	0.145	0.255	0.111	0.221
148	0.071	0.240	0.125	0.233	0.108	0.216

Parameter Estimation with MatLab

For completeness, two different approaches and object functions were implemented into MatLab, for the evaluation of the example case: 1. Fit to the pre-processed data of S_{eq} - S_{neq} and 2. Fit to M_t - $C_{l\,des}$, similar to the approach used in PEARLNEQ. In this example all residue data are equally weighted.

S_{eq} - S_{neq} approach
As the two equilibrium phase concentrations C_l and S_{eq} are directly dependant via the Freundlich isotherm, the corresponding equations can be written in terms of only one variable. Thus, the object function for optimisation is represented by a set of two differential equations of either C_l or S_{eq} together with S_{neq}, where for the example here S_{eq} was chosen. For a full description of this approach including the pre-processing and the derivation of the object function based on the PEARL two-site (kinetic) sorption model (see Kley and Hammel, 2008).

The result file of the MatLab optimisation is shown in Table A6-10. A summary of the results is given in Table A6-11 and graphs of fits for the equilibrium phase concentration of soil S_{eq} and non-equilibrium phase concentration of soil S_{neq} are given in Figure A6-9.

Table A6-10. Results of parameter fitting with MatLab for the example case, using the S_{eq} - S_{neq} approach.

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Model parameters

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Initial values model parameters

Name	Value	Fixed	
1/n	0.9	1	Freundlich exponent
M_app	0.5	1	Applied substance mass [µg]
M_soil	0.5	1	Soil dry mass [g]
theta_g	0.1492	1	Gravimetric water content during incubation [g water/g soil]
Vw_add	0.5	1	Water volume added for desorption [mL]
Kf_eq	2.586	1	Freundlich coefficient, in equilibrium domain [L/kg]
k_t	0.01	0	Degradation rate in equilibrium domain [1/d]
k_d	0.01	0	Sorption rate [1/d]
f_ne	0.5	0	Ratio of Kf_eq / Kf_neq

Initial values state variables

S_eq0(t=0)	0.95	0	Conc. in equilibrium sorbed phase at t=0 [mg/kg]
S_neq0(t=0)	0	1	Conc. in non-equilibrium sorbed phase at t=0 [mg/kg]

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Optimization results

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	estimate	standard deviation	95% probability of T-test	coefficient of variation
k_t in 1/d	0.0078	0.0002	0.0000	3.13%
k_d in 1/d	0.0135	0.0012	0.0000	8.75%
f_{ne}	0.6650	0.0311	0.0000	4.68%
S_{eq_0}, mg/kg	0.9527	0.0080	0.0000	0.84%
$DT50_{eq}$ in d	89.07	2.7838		3.13%
M_{t0} in µg	0.5009	0.0042		0.84%

Chi^2 Errors, in %

	Unweighted	Weighted
S_eq	0.61	0.61
S_neq	7.73	7.73
Total	2.43	2.43

_____

Table A6-10 (continued). Results of parameter fitting with MatLab for the example case, using the S_{eq} - S_{neq} approach.

Correlation Matrix

	k_t	k_d	f_ne	S_eq0(t=0)
k_t	1	0.238008332	-0.245762028	0.633430682
k_d	0.238008332	1	-0.843107693	0.308487719
f_ne	-0.245762028	-0.843107693	1	-0.234563818
S_eq0(t=0)	0.633430682	0.308487719	-0.234563818	1

Measured and predicted values

Time	S_eq	Calculated S_eq	Residuals S_eq
d	µg/g	µg/g	µg/g
0	0.959770562	0.952692879	0.007077683
7	0.8485002	0.852786599	-0.004286399
14	0.763283923	0.76768075	-0.004396827
28	0.630754819	0.632746249	-0.001991431
61	0.441946438	0.436487003	0.005459435
90	0.341878095	0.3414556	0.000422495
120	0.276961744	0.279743341	-0.002781596
148	0.240246224	0.239674976	0.000571248

Time	S_neq	Calculated S_neq	Residuals S_neq
d	µg/g	µg/g	µg/g
0	-0.028164916	0	-0.028164916
7	0.058041026	0.053980714	0.004060312
14	0.085839302	0.097571482	-0.01173218
28	0.175412056	0.160291392	0.015120664
61	0.212552963	0.226122701	-0.013569738
90	0.236729083	0.235146475	0.001582607
120	0.221423659	0.224694415	-0.003270756
148	0.215547704	0.207864567	0.007683137

Table A6-11. Summary of parameter fitting with MatLab for the example case, using S_{eq} - S_{neq} approach.

	estimate	standard deviation	95% probability of T-test	coefficient of variation
k_t in 1/d	0.0078	0.0002	0.0000	3.13%
k_d in 1/d	0.0135	0.0012	0.0000	8.75%
f_{ne}	0.6650	0.0311	0.0000	4.68%
S_{eq_0}, mg/kg	0.9527	0.0080	0.0000	0.84%
$DT_{50,eq}$ in d	89.07	2.7838		3.13%
$M_{t\,0}$ in µg	0.5009	0.0042		0.84%

Figure A6-9. Fitted graphs of example case, using S_{eq} - S_{neq} approach.

M_t - $C_{l\,des}$ approach

For comparison, the same object function as in Pearlneq was implemented into MatLab, i.e. fits were made to the experimental data of M_t and $C_{l\,des}$. A summary of the results is given in Table A6-13, detailed results in A6-14 and graphs of fits for total substance mass M_t and concentration in the desorption solution $C_{l\,des}$ are given in Figure A6-10.

Table A6-12. Summary of parameter fitting with MatLab for the example case, using M_t - $C_{l\,des}$ approach

	estimate	standard deviation	95% probability of T-test	coefficient of variation
k_t in 1/d	0.0076	0.0002	0.0000	2.08%
k_d in 1/d	0.0126	0.0022	0.0004	17.68%
f_{ne}	0.6783	0.0657	0.0000	9.68%
S_{eq_0}, mg/kg	0.9436	0.0045	0.0000	0.48%
$DT_{50,eq}$ in d	91.40	1.8965		2.08%
$M_{t\,0}$ in µg	0.4962	0.0024		0.48%

Table A6-13. Results of parameter fitting with MatLab for the example case, using M_t - $C_{l\,des}$ approach.

Report Model optimization   Date: 11.04.2008

Model name: KinSorp Version 1.0 2007, MatLab R2007b

Compound: **example**   **Fit results to Mtotal - Cl_des**

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Model parameters
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Initial values model parameters

Name	Value	Fixed	
1/n	0.9	1	Freundlich exponent
M_app	0.5	1	Applied substance mass [μg]
M_soil	0.5	1	Soil dry mass [g]
theta_g	0.1492	1	Gravimetric water content during incubation [g water/g soil]
Vw_add	0.5	1	Water volume added for desorption [mL]
Kf_eq	2.586	1	Freundlich coefficient, in equilibrium domain [L/kg]
k_t	0.01	0	Degradation rate in equilibrium domain [1/d]
k_d	0.01	0	Sorption rate [1/d]
f_ne	0.5	0	Ratio of Kf_eq / Kf_neq

Initial values state variables			
S_eq0(t=0)	0.95	0	Conc. in equilibrium sorbed phase at t=0 [mg/kg]
S_neq0(t=0)	0	1	Conc. in non-equilibrium sorbed phase at t=0 [mg/kg]

_____

Optimization results
_____

	estimate	standard deviation	95% probability of T-test	coefficient of variation
k_t in 1/d	0.0076	0.0002	0.0000	2.08%
k_d in 1/d	0.0126	0.0022	0.0004	17.68%
f_{ne}	0.6783	0.0657	0.0000	9.68%
S_{eq_0}, mg/kg	0.9436	0.0045	0.0000	0.48%
$DT50_{eq}$ in d	91.40	1.8965		2.08%
$M_{t\,0}$ in μg	0.4962	0.0024		0.48%

Chi^2 Errors, in %

	Unweighted	Weighted
Mtotal	1.18	1.18
Cl_des	1.03	1.03
Total	1.22	1.22

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Table A6-13 (continued). Results of parameter fitting with MatLab for the example case, using M_t - $C_{l\,des}$ approach.

Correlation Matrix

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	k_t	k_d	f_ne	S_eq0(t=0)
k_t	1	0.274549726	0.029433769	0.671162337
k_d	0.274549726	1	-0.868703956	0.159108759
f_ne	0.029433769	-0.868703956	1	-0.027537177
S_eq0(t=0)	0.671162337	0.159108759	-0.027537177	1

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Measured and predicted values

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Time	M_total	Calculated M_total	Residuals M_total
d	µg/g	µg	µg
0	0.490602654	0.496152206	-0.005549552
7	0.474897155	0.471189382	0.003707773
14	0.443788719	0.448714787	-0.004926068
28	0.418638994	0.409878473	0.008760521
61	0.337726508	0.340842568	-0.00311606
90	0.297180245	0.296271615	0.00090863
120	0.255426161	0.259445986	-0.004019825
148	0.233219313	0.230691907	0.002527406

Time	Cl_des	Calculated Cl_des	Residuals Cl_des
d	µg/g	µg/mL	µg/mL
0	0.244624783	0.240170079	0.004454704
7	0.214043703	0.213894173	0.00014953
14	0.190843056	0.191532375	-0.000689319
28	0.155192812	0.156124899	-0.000932087
61	0.105507335	0.10480035	0.000706985
90	0.079848608	0.080163631	-0.000315023
120	0.06352878	0.064408677	-0.000879897
148	0.054436049	0.054394088	4.19614E-05
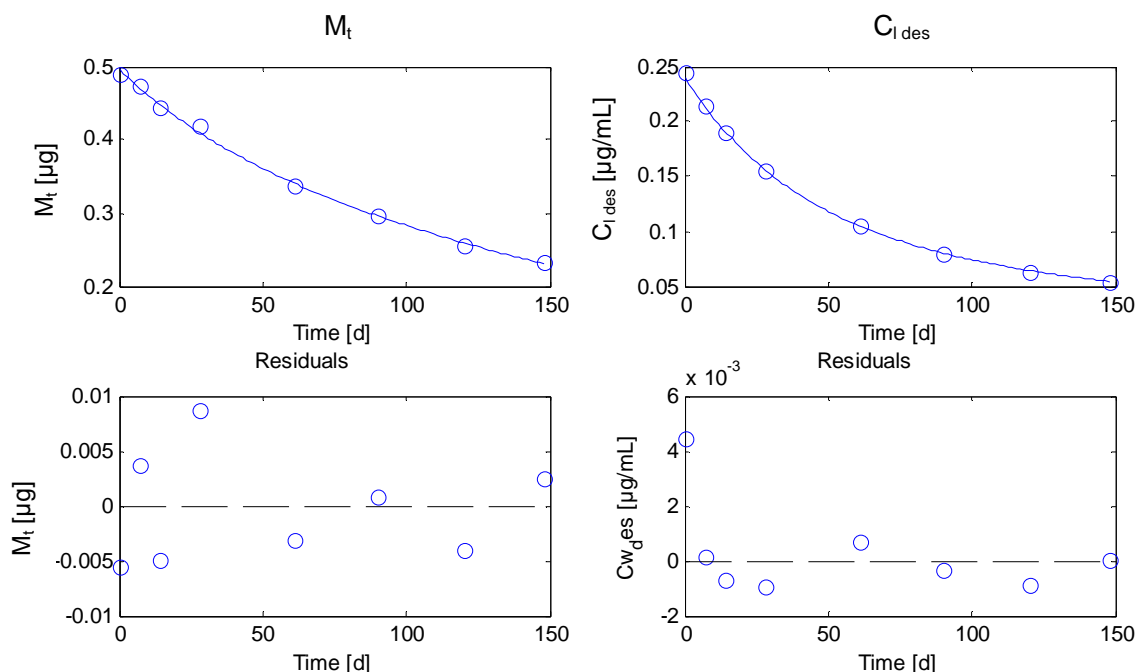
Figure A6-10. Fitted graphs of example case, using M_t - $C_{l\,des}$ approach.

Comparison of the Estimated Non-equilibrium Sorption Parameters Using Different Tools and object functions

The comparison of the estimated parameters and its standard deviation is shown in Table A6-14. The results in Table A6-14 show that all software packages resulted in fitted f_{NE} and k_d values that are close to the true values (i.e. $f_{NE} = 0.7$ and $k_d = 0.012$ d-1 as given in Table A6-1). Comparing the fit to M_t and $C_{l\,des}$, the results of all fitting tools, PEARLNEQ, ModelMaker and MatLab are almost identical. Considering the fit to S_{eq} and S_{neq}, the results show also only slight differences. This is probably a result of the different object function, which may be more or less sensitive to the dynamic of the system. In this example case, the S_{eq} - S_{neq} approach with MatLab generates lower standard deviations for the sorption kinetic parameters f_{NE} and k_d compared to the M_t and $C_{l\,des}$ approach. In general, there should be no difference between the different object functions in the reliability of the optimised parameters. Thus, slight deviations of estimated parameters and coefficients of variation are likely to be coincidental. However, fits to different object functions can be comparable only under assumption that the parameters are mathematically reliable, i.e. significantly different from 0 (t-test). In less stable experimental systems, the estimated parameters may differ significantly between the different fit approaches. To examine this hypothesis of equivalence

a numerical experiment was carried out (Appendix 25), using the M_t - $C_{l\,des}$ and the S_{eq} - S_{neq} approach.

Table A6-14. Comparison of parameters estimated with PEARLNEQ, ModelMaker 3.0 and MatLab and different object functions

	Parameter	f_{NE}	k_d	DegT50$_{eq}$	$M_{t\,0}$
			1/d	d	µg
M_t - $C_{l\,des}$	approach				
PEARLNEQ	Estimated value	0.681	0.0125	91.4	0.496
	standard deviation	0.0662	0.00222	1.90	0.00240
	CV (%)	9.73	17.7	2.07	0.484
ModelMaker	Estimated value	0.681	0.0125	91.4	0.496
	standard deviation	0.0659	0.00222	1.91	0.00240
	CV (%)	9.68	17.7	2.09	0.483
MatLab	Estimated value	0.678	0.0126	91.4	0.496
	standard deviation	0.0657	0.0022	1.90	0.0024
	CV (%)	9.68	17.7	2.08	0.48
S_{eq} - S_{neq}	approach				
MatLab	Estimated value	0.665	0.0135	89.1	0.501
	standard deviation	0.0311	0.0012	2.78	0.0042
	CV (%)	4.68	8.75	3.13	0.84

In the present example case the SFO fit of the total mass results in a DegT50$_{tot}$ of 130.2 days as shown in Figure A6-11, and therefore the scaling factor f_{deg_NE} (defined by Equation 7-29) is found to be 0.70 which can be applied to all DegT50$_{tot}$ values. The value for f_{deg_NE} estimated following the approximation of Boesten and van der Linden (2001) would be 0.60 (using Equation 7-31) and thus less conservative than the directly derived factor using the compound specific properties.

If field studies are used, the re-calculation of the DegT50$_{tot}$ under consideration for non-equilibrium sorption requires an extended version of the software tools, since the variation in changing temperature and moisture conditions of outdoor degradation studies would have to be considered. Instead of PEARLNEQ, FOCUS-PEARL should be directly linked with PEST. The ModelMaker and MatLab approach requires an extension with moisture and temperature dependency as shown in Gurney et al. (2007) and Kley and Hammel (2008).

FOCUS_DEGKIN v1
Visual assessment and chi2-test for SFO kinetics
For datasets without replicates
Change number of parameters if M0 was fixed in optimisation!

User input, all other cells calculated

Name of dataset: **Example dataset 1**

No	Time	Observed	Calculated	SFO parameters and endpoints			
1	0	98.12	97.09	M0	97.09	DT50	130.2
2	7	94.98	93.53	k	0.005	DT90	432.4
3	14	88.76	90.11				
4	28	83.73	83.64				
5	61	67.55	70.16				
6	90	59.44	60.12				
7	120	51.09	51.24				
8	148	46.64	44.14				

Figure A6-11. SFO fit of the total mass (see Table A6-2) of the example case with FOCUS_DEGKIN v1.

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APPENDIX 7. EXAMPLE CALCULATION OF DegT50$_{eq}$ FROM A LABORATORY DEGRADATION RATE STUDY BASED ON DEFAULT VALUES OF THE NON-EQUILIBRIUM SORPTION PARAMETERS

J. Boesten and C. Kley

Section 7.1.6 recommends the recalculation of the *DegT50* if default values of parameters describing long-term sorption kinetics (so $k_{d,PEARL} = 0.01$ d^{-1}, f$_{NE,PEARL} = 0.3$) are included in the leaching assessment. This appendix provides an example of such a calculation.

The data for the laboratory study were "generated" by calculations with the system of Equations 7-3 to 7-7 using the following parameter values: $K_{F,EQ} = 1.0$ L/kg, $\theta = 0.2$ (volumetric), $\rho = 1$ kg/L, $c_{L,R} = 1$ mg/L, $N = 0.9$, $k_{d,PEARL} = 0.01$ d^{-1}, f$_{NE,PEARL} = 0.5$, *DegT50$_{eq}$* = 30 d, which corresponds to $k_t = \ln(2)/30 = 0.023$ d^{-1}. The calculation procedure was as described by Boesten et al. (2007). Nine data points for the times 0, 10, 20, .., 70 and 80 d were calculated. Two series of calculations were made: in the first it was assumed that the data points were free of errors, and in the second it was assumed that the concentration in total soil was normally distributed with a coefficient of variation of 3 % (see Table A7-1 for values). The value of f$_{NE,PEARL}$ was set to 0.5 for generation of the data points because this is considered a "best guess" value (Leistra et al., 2001). Only results of the concentration in total soil were used (and no pore water concentrations) because pore water concentrations are not available in a case where default values of the parameters for long-term sorption kinetics are used. Therefore, the case considered here is a soil incubation study where the decline of the concentration in total soil was measured but with no measurements of pore water concentrations. The example was based on hypothetical data because this has the advantage that the true parameter values of the system are known.

Table A7-1. Generated data points for illustrating the fitting procedure of *DegT50$_{eq}$*.

Time (days)	Concentration in total soil (mg/kg)	
	No experimental error	**Error based on CV of 3 %**
0	1.0000	1.0363
10	0.7976	0.7757
20	0.6429	0.6666
30	0.5240	0.5470
40	0.4320	0.4388
50	0.3605	0.3497
60	0.3043	0.3066
70	0.2598	0.2540
80	0.2242	0.2143

These data were fitted back to the model described by Equations 7-3 to 7-7 using the PEST optimisation package (Boesten et al., 2007) and a MatLab software package (Kley and Hammel, 2008; MatLab, 2007). In this fitting procedure, only the initial concentration in soil and the *DegT50$_{eq}$* were fitted. All other parameters were kept fixed. Table A7-2 shows the PEST pst file used to perform this fitting procedure. As described above, this appendix considers the case where default parameter values for the long-term sorption parameters are used (so $k_{d,PEARL}$ = 0.01 d^{-1}, $f_{NE,PEARL}$ = 0.3). Section 7.1.6 recommends using these default parameters also for fitting the *DegT50$_{eq}$*. For illustrative purposes, here the *DegT50$_{eq}$* was also estimated using fixed $f_{NE,PEARL}$ values of 0 and 0.5.

Table A7-2. Example of PEST pst file for fitting back the data shown in Table A7-1 to Equations 7-3 to 7-7.

```
pcf
* control data
restart
  2  9  2 0
1 1 single point
5.0 2.0 0.4 0.03 10
3.0 3.0 1.0e-3
0.1
30 0.01 3 3 0.01 3
1 1 1
* group definitions and derivative data
DT50   relative 0.01  0.0  switch  2.0 parabolic
MASINI relative 0.01  0.0  switch  2.0 parabolic
* parameter data
DT50   none relative     14.0000  1.0  500.0  DT50   1.00  0.00
MASINI none relative      1.400   0.0 1000.0  MASINI 1.00  0.00
* observation data and weights
o1     1.036  1.00
o2     0.776  1.00
o3     0.667  1.00
o4     0.547  1.00
o5     0.439  1.00
o6     0.350  1.00
o7     0.307  1.00
o8     0.254  1.00
o9     0.214  1.00
* model command line
..\neq_bin\PearlNeq example
* model input/output
example.tpl   example.neq
example.ins   example.out
```

Figures A7-1 and A7-2 show that all fitted lines describe the generated data points very well and that there is almost no difference between the lines for the different $f_{NE,PEARL}$ values, shown here for the PEST evaluation.

For the PEST evaluation, Table A7-3 shows that true value for $DegT50_{eq}$ of 30 d was indeed estimated for $f_{NE,PEARL}$ = 0.5 for the data points without experimental error (this fit was simply a consistency check). The table shows also that the $DegT50_{eq}$ value increases with decreasing $f_{NE,PEARL}$ values, as would be expected from the description in Section 7.1.6. The table shows also that the resulting $DegT50_{eq}$ values were similar for the data points that included an experimental error with a CV of 3 %.

Very similar values and observations were made using the MatLab software package, which is shown in Table A7-4. Marginal differences might be caused by different fitting algorithms. Therefore, both software packages can be considered equivalent.

Section 7.1.6 also contains an approximation for estimating the effect of $f_{NE,PEARL}$ on the fitted *DegT50$_{eq}$* value (Equation 7-31). This equation was used to estimate the *DegT50$_{eq}$* from the *DegT50$_{tot}$* of 34.9 d (i.e., the value found with $f_{NE,PEARL}$ = 0.0 in Tables A7-2 and A7-3). This resulted in a *DegT50$_{eq}$* of 25 days which is 16 percent shorter than the true value of 30 days. As described in Section 7.1.6, Equation 7-31 was derived assuming that the degradation rate coefficient k_t was considerably slower than the adsorption/desorption rate coefficient of the long-term sorption sites, $k_{d,PEARL}$. A *DegT50$_{eq}$* of 30 days corresponds to a k_t of 0.023 d^{-1} and whereas $k_{d,PEARL}$ was 0.01 d^{-1}, so this assumption was not valid in this case.

Table A7-3. Fitted values of DegT50eq and their 95 % confidence intervals as calculated by the PEST software package.

$f_{NE,PEARL}$	*DegT50$_{eq}$* (d)			
	no experimental error		error based on CV of 3 %	
	fitted value	95 % confidence interval	fitted value	95 % confidence interval
0	34.9	32.8-37.0	34	31-37
0.3	31.8	31.0-32.5	31	29-33
0.5	30.0	29.9-30.0	29	27-31

Table A7-4. Fitted values of DegT50eq and their 95 % confidence intervals as calculated by the MatLab software package. A normal distribution was assumed: 95.4 % confidence interval = mean ± 2 x standard deviation.

$f_{NE,PEARL}$	*DegT50$_{eq}$* (d)			
	no experimental error		error based on CV of 3 %	
	fitted value	95 % confidence interval	fitted value	95 % confidence interval
0	34.9	33.2 - 36.8	34.1	31.9 - 36.5
0.3	32.2	31.5 - 33.1	31.4	29.8 - 33.3
0.5	30.6	30.4 - 30.9	29.9	28.3 - 31.6
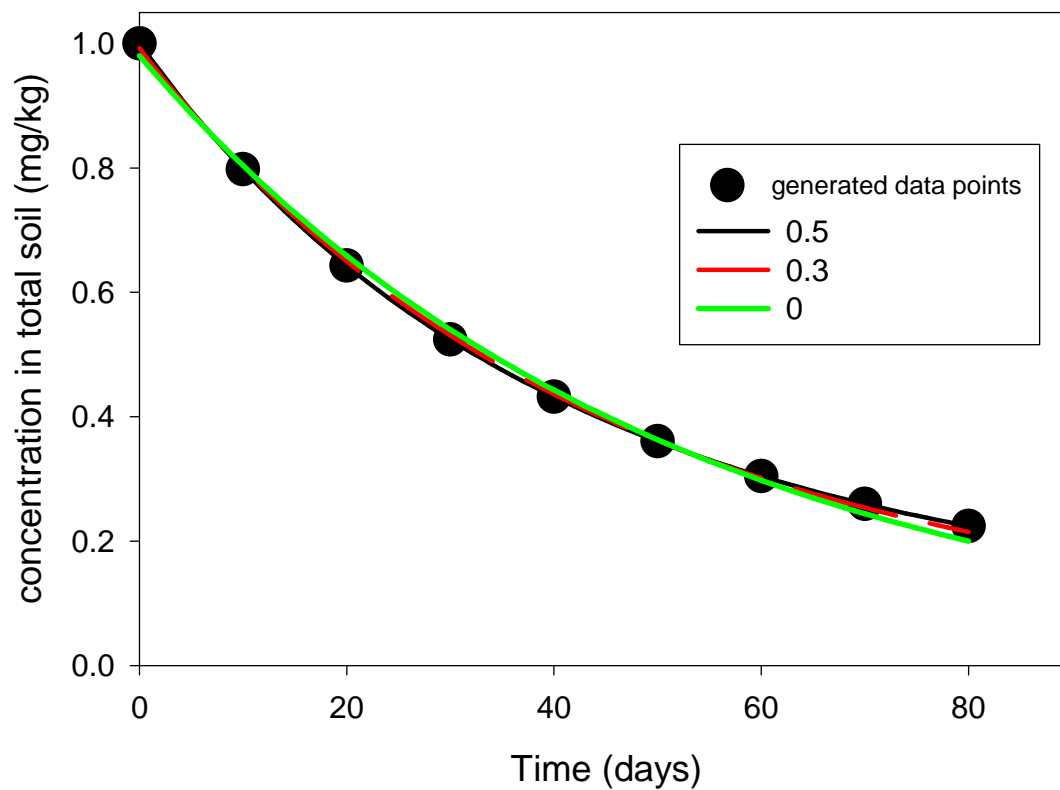
Figure A7-1. Time course of concentration in total soil in hypothetical laboratory degradation rate study. Points are generated data points assuming no experimental error and the three lines are the fits from PEST of the model to the data with fixed values of $f_{NE,PEARL}$ as indicated in the graph.
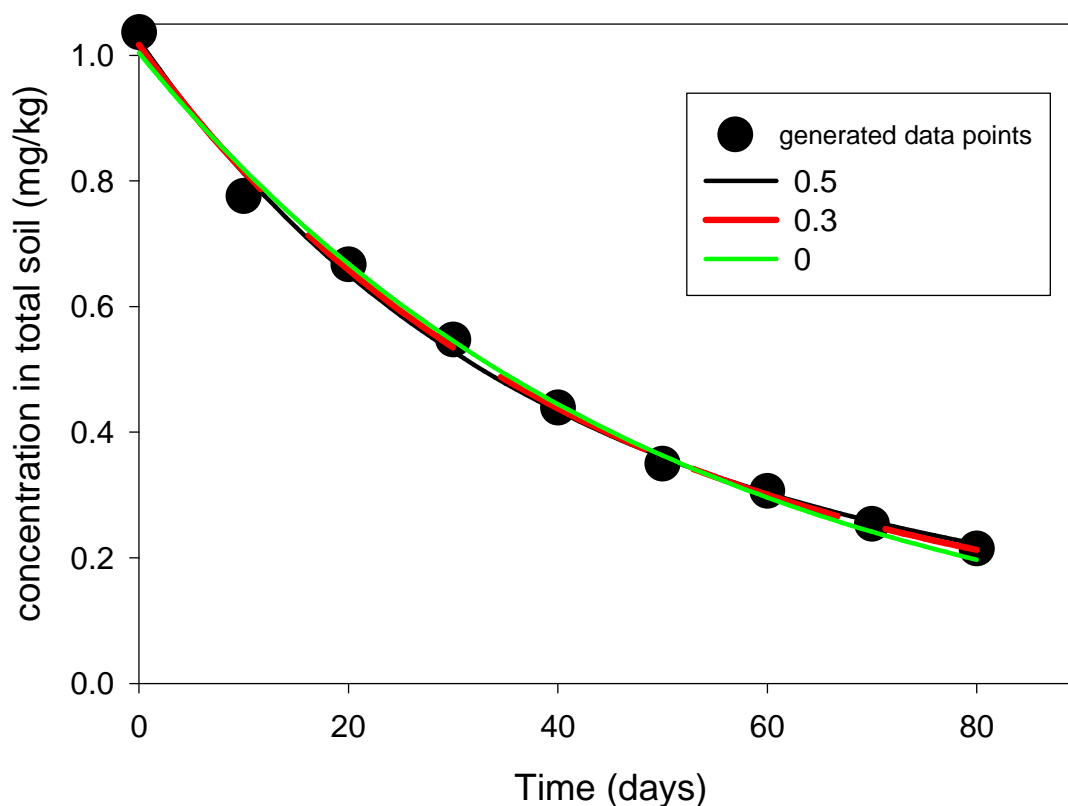
Figure A7-2. Time course of concentration in total soil in hypothetical laboratory degradation rate study. Points are generated data points assuming an experimental error corresponding with a CV of 3 % and the three lines are the fits from PEST of the model to the data with fixed values of $f_{NE,PEARL}$ as indicated in the graph.

This example shows that estimating the *DegT50$_{eq}$* from degradation studies in the laboratory is in principle quite straightforward, using either the PEST or the MatLab software packages and that these two software packages gave almost exactly the same results.

References

Boesten JJTI, Tiktak A & Van Leerdam RC. 2007. Manual of PEARLNEQ 4. Working document 71. Statutory Research Tasks Unit for Nature & the Environment. Alterra, Wageningen, The Netherlands.

Kley, C. and Hammel, K. 2008. Evaluation of Time-dependent Sorption Parameters based on concentrations in unsaturated soil. Bayer CropScience AG, Metabolism and Environmental Fate, Monheim am Rhein, Germany. Report No: MEF-07/429. (available upon request from K. Hammel, klaus.hammel@bayercropscience.com).

Leistra M, van der Linden AMA, Boesten JJTI, Tiktak A, van den Berg F. 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 13, Alterra, Wageningen, the Netherlands.

MatLab. 2007. MatLab Version 7.4.0.287 (R2007a), Optimisation Toolbox, Statistics Toolbox, MatLab Compiler. The MathWorks Inc., USA. www.mathworks.com

APPENDIX 8. FACT SHEETS FOR REGIONAL DATA

This appendix includes information on the following data bases or maps:

> CORINE Land Cover
>
> European Soil Map
>
> European Groundwater Map
>
> IPCC Global Climate Data
>
> Digital Elevation Model
>
> Administrative Boundaries (AD)
>
> European Zonal Map
>
> European Census Data (AD)
>
> MARS Climate Data Base
>
> Irrigation Data Base
>
> The Map of Organic Carbon in Topsoils in Europe

CORINE Land Cover

Description

The CORINE land cover data set was developed by the European Environment Agency as part of the CORINE Program (Coordination of Information on the Environment) to provide a consistent land cover data set at a reasonable resolution across the European Union. The first version of Corine Land Cover – CLC1990 – reflected land use in Europe between 1986 and 1995, depending on the production date of the underlying satellite images. In the meantime a new version – CLC2000 – is being prepared for release. The updated version shows land use in Europe in 2000 (+/- 1 year). Table A8-1 and Figure A8-1 give an overview about the progress of the CLC 2000 project as of May 2004. Currently Corine covers all of the European Union.

Table A8-1. Status of Corine Land Cover 2000 as of May 2004

Available	Not available, partial delivery
Estonia	Belgium
Ireland	Czech Republic
Latvia	France
Lithuania	Germany
Luxembourg	Hungary
Malta	Poland
Slovenia	Romania
The Netherlands	Slovakia
	Sweden

- EU Member States except Sweden
- Acceding countries except Malta and Cyprus
- Romania, Bulgaria
- Albania, Bosnia, Macedonia, Tunisia and Morocco
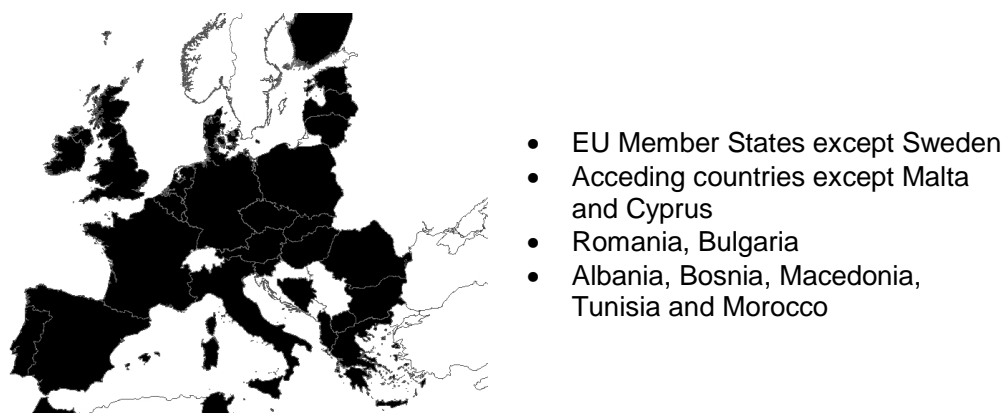
Figure A8-1. Spatial extent of current Corine Land Cover data (CLC1990/2000); version of May 2004.

Content

Land use was mapped by means of computer assisted classification of satellite scenes with the simultaneous consultation of ancillary data such as topographic maps. Note that the minimum classification accuracy varied from 10 x 10 m to 30 x 30 m depending on the satellite sensor. As a pragmatic solution the minimum cartographic unit was set to 25 ha. The minimum width of linear features was 100 m. In this way land use patterns smaller than 25 ha or linear features with a width of < 100 m were grouped together with the dominant surrounding land use pattern. In total 45 land use classes are provided by CORINE Land Cover. Eleven classes are particularly relevant for environmental risk assessments for pesticides (Table A8-2).

Table A8-2. CORINE Land Cover classes for agricultural areas.

Corine Grid Code	Corine Legend Class	Level 1	Level 2	Level 3
12	2.1.1	Agricultural areas	Arable land	Non-irrigated arable land
13	2.1.2	Agricultural areas	Arable land	Permanently irrigated land
14	2.1.3	Agricultural areas	Arable land	Rice fields
15	2.2.1	Agricultural areas	Permanent crops	Vineyards
16	2.2.2	Agricultural areas	Permanent crops	Fruit trees and berry plantations
17	2.2.3	Agricultural areas	Permanent crops	Olive groves
18	2.3.1	Agricultural areas	Pastures	Pastures
19	2.4.1	Agricultural areas	Heterogeneous agricultural areas	Annual crops associated with permanent crops
20	2.4.2	Agricultural areas	Heterogeneous agricultural areas	Complex cultivation patterns
21	2.4.3	Agricultural areas	Heterogeneous agricultural areas	Land principally occupied by agriculture, with significant areas of natural vegetation
22	2.1.1	Agricultural areas	Heterogeneous agricultural areas	Agro-forestry areas

A detailed definition of each class is given in Bossard et al. (2000) therefore the following chapter highlights only a few characteristics of CORINE Land Cover that have to be considered when using the data set in spatial risk assessments for agrochemicals.

Class 2.1.1, Non-irrigated arable land

The class includes field crops, tree nurseries and vegetables with more than 75 % of the area under a rotation system. Also semi-permanent crops like strawberries or sugar cane are included in this class as well as large areas under greenhouse cultivation. Arable land is classified as a general feature and thus does not allow for the visualization of specific crops. A particularity of this class is that fallow land (= not cropped for 1 – 3 years) is included because it forms part of a rotation system.

Class 2.1.2, Permanently irrigated land

Crops, which are permanently, irrigated using a permanent infrastructure (irrigation channels, drainage network). The class excludes sporadically irrigated land as well as rice fields and greenhouses

Class 2.1.3, Rice fields

Land prepared for rice cultivation and adjacent irrigation channels

Class 2.2.1, Vineyards

Areas planted with vines for wine, consumer grapes and raisin production. The class includes all complex cultivation patterns were vineyard parcels cover at least 50 % of the area.

Class 2.2.2, Fruit trees and berry plantations

Parcels planted with fruit trees or shrubs. This class includes also hops and other permanent crops like permanent horticultural plantations. In case of equal occurrence with vineyards and olive groves priority was given to these crops.

Class 2.2.3, Olive groves

Areas planted with olive trees including mixed occurrence with vines on the same parcel.

Class 2.3.1, Pastures

This class includes also abandoned arable land, which is not part of a rotation system (> 3 years fallow). Patches of arable land that cover less than 25 % of a minimum mapping area of 25 ha and is surrounded by pastures is classified as 'pasture'.

Class 2.4.1, Annual crops associated with permanent crops

All complex cultivation patterns where non-permanent crops occupy more than 50 % of area.

Class 2.4.2, Complex cultivation patterns

Juxtaposition of small parcels of diverse annual crops, pasture and/or permanent crops. This class includes also scattered houses and roads that cover < 30 % of the patchwork structure.

Class 2.4.3, Land principally occupied by agriculture with significant areas of natural vegetation

This class includes parcels of arable land, orchards and vineyards < 25 ha which were not grouped under one of the previous classes.

Class 2.4.4, Agro-forestry areas

Annual crops or grazing land under the wooded cover of forestry species.

General considerations for environmental risk assessments of pesticides

In some regions the majority of arable land is found in complex cultivation systems with natural vegetation, permanent crops and pastures. Due to a minimum mapping unit of 25 ha deriving *e.g.* the acreage of arable land from Corine Land Cover is not possible because of generalization errors. Nevertheless Corine Land Cover represents currently the most accurate data source on land use in the EU. Corine Land Cover should be used for the identification of agricultural areas vulnerable to pesticide leaching since a satellite based land use map excludes non-agricultural areas with a sufficient degree of accuracy.

Data distribution

A 250-m grid can be acquired free of charge from the European Environment Agency (http://dataservice.eea.eu.int/dataservice/). The data layer is available in commonly used GIS-formats (e.g. ArcInfo Export file, Imagine Raster format).

Higher resolution versions of CORINE Land Cover (e.g. 100-m) can be obtained on request from European Topic Center on Land Cover (ETC/LC) distributed by Environmental Satellite Data Center (MDC Environmental Satellite Data Center, Miljodatacentrum I Kiruna AB, PO Box 806, SE-981 28 Kiruna, Sweden, Tel: +46 0980-671 70, Fax: 0980-671 80, Email: mdc@mdc.kiruna.se, Internet: www.mdc.kiruna.se).

Documentation

The most comprehensive documentation about the current version of Corine Land Cover is provided on the website of the European Topic Center on Terrestrial Environment of the European Environment Agency (http://terrestrial.eionet.eu.int/CLC2000).

- Corine Land Cover update I&CLC2000 project Technical Guidelines. Final version August 2002. European Environment Agency. European Topic Center Terrestrial Environment.
- Bossard M., Feranec J. and J. Otahel. 2000. Corine Land Cover technical guide – Addendum 2000. Technical Report No. 40. European Environment Agency.
- Technical and methodological guide for updating the Corine Land Cover Data Base. Joint Research Center, EU Commission, European Environment Agency. Report No. EUR 17288 EN.

European Soil Map

General Information

The Soil Geographical Data Base of Europe at scale 1 : 1,000,000 contains the spatial extension and major properties of soil units in the European Union and neighbouring countries. Soils are mapped as Soil Mapping Units (SMU), which do not correspond to individual soil types but soil associations. Each SMU might contain a number of Soil Typological Units (STU), which were classified in accordance to the FAO legend for the Soil Map of the World (FAO, 1975). The attribute table for STU's contains information about general soil properties like texture class or water regime. Each SMU is composed of 1 to 10 STU's, which cover a certain area of the SMU. The spatial extent of STU's is not delineated in the map but is given in tabular form as percentage of SMU covered by a specific STU. Additional tables with a more detailed description of soil properties can be linked with the soil map.

- EU Member States
- Acceding countries except Malta and Cyprus
- Romania, Bulgaria
- Albania, Bosnia, Macedonia, Croatia, Serbia and Montenegro, Norway, Switzerland
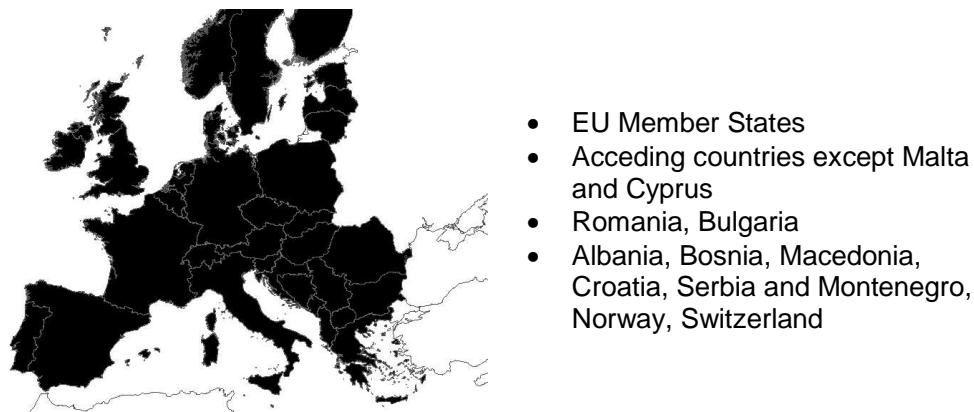
Figure A8-2. Spatial extent of the European Soil Map

Content

The Soil Geographical Data Base of Europe contains a base map with Soil Mapping Units (SMU) and a number of attribute tables that can be linked with the base map. Each SMU contains one or more Soil Typological Units (STU). The fraction of an SMU that is covered by an STU is given in the table STU.ORG.dbf. Linking STU.ORG with the attribute table of the base map allows linking basic soil property information with the base map. The primary

identification code of all attribute tables is always the STU-code. The following sections briefly describe the attribute tables of the main data bases:

Soil Geographical Data Base

STU.ORG.dbf: This table is the link between the base map and any of the following attribute tables. STU.ORG assigns STU's to each SMU along with the percentage of area (PCAREA) that is covered by the STU within a SMU.

STU.dbf: STU.dbf is the primary attribute table and contains the FAO soil name, information about parent material, soil depth and some general soil properties, which are provided as class values. In this way most of the crucial soil properties that are required for leaching simulations are not given as absolute numbers and cannot be used directly as input parameters in environmental fate models.

Pedotransfer Rule Data Base

STU.dbf: The pedotransfer rule data base provides additional information that was derived on the basis of existing information stored in the Soil Geographical Data Base. The most relevant parameters for the assessment of leaching risk are organic carbon contents in topsoil, available water capacity and depth to impermeable layers. Again most parameters are given in qualitative form or as class-values.

Soil Profile Analytical Data Base (SPADE-1)

Est_prof2stu.lnk.dbf: This table stores the required links between STU's and the information stored in the Soil Profile Analytical Data Base.

Est_prof.dbf: The estimated profile table contains more detailed information like depth to ground water and parent material for selected soil units. A link is provided to STU's by using est_prof2stu.lnk.dbf.

Est_hor.dbf: The estimated horizon table gives estimated soil properties for each horizon of soils shown in Est_prof.dbf. This table contains absolute values for crucial soil properties and is **thus the primary source for input parameters that are required for leaching simulations**. The total number of estimated soil profiles varies significantly between countries. Some countries (e.g. Austria) are not represented at all by an estimated soil profile, whereas others provide only a very limited number of profiles. An important attribute is the dominant land use (LU) of the estimated soil profile. The current version of Est_hor.dbf contains only a limited number of soil

profiles with 'arable land' or 'perennial crop' as dominant land use. In leaching modelling studies profile data from agricultural soils must be used in order to avoid the co-occurrence of unrealistic combinations of factors.

The SPADE-1 data base, which is delivered with the current version of the European soil map, contains 447 estimated soil profiles among which 240 are linked to STU`s (8 % of the total number of STU`s. The total number of STU`s in the 15 EU member states before 2004 is 3164, among those 1206 STU`s have a designated dominant land use of "arable land". In total only 78 STU`s (6%) representing arable land are actually linked to SPADE-1.

In the light of these deficiencies the European Crop Protection Association, supported by the European Soil Bureau of the European Commission's Joint Research Centre, sponsored the compilation of a second version (SPADE-2) of the profile data base for use with the Soil Geographical Database of Europe. SPADE-2 contains additional soil profiles for Belgium, Luxemburg, Denmark, Italy, the Netherlands, Portugal and Scotland. Other member states either declined to supply data or could not provide the requested data within the project time-frame. The new data base contains 1897 complete profiles which are directly linked to 1077 STU`s.

The SPADE-2 database will be distributed in the future as part of the European Soil Database version 3.0. The SPADE.dbf and SPADE_2_raw.xls containing the original national data are included for circulation on a CD available with the final report of the project (Hollis et al. 2006). The report and the CD Rom are available through the Office for Official Publications of the European Communities in Luxembourg.

Note that all examples for higher-tier GIS work in this report were conducted with SPADE-1 since SPADE-2 was not available to the FOCUS work group at the time when this report was written.

Meas_prof: The Soil Analytical Data Base contains also measured soil profile data from various countries with a varying degree of completeness. There is no direct link between measured soil profiles and any other attribute table therefore this data base should not be used as source for input parameters in leaching simulations.

HYPRES Data Base of Hydraulic Properties of European Soils

`PARAM.doc:` The HYPRES data base consists of a small number of pedotransfer functions and parameters that are stored in a word document. The hydraulic parameters were derived on the basis of European soils and were adapted to the existing parameter structure of in the European Soil Map. The data are provided in two different ways. Class pedotransfer functions can be used in combination with STU.dbf to visualize hydraulic properties for whole Europe. Continuous pedotransfer functions are finally used to derive hydraulic parameters for soil horizons as required for leaching modelling studies.

General considerations for environmental risk assessments of pesticides

A number of soil properties are available as class values for almost all STU's (except developed land and some mountainous areas). European-wide maps can be derived showing soils that *e.g.* belong to a certain texture class or a class of organic carbon contents in topsoil.

Only a limited number of STU's have data that describe soil horizons and are required for leaching simulations. The attribute table Est_hor.dbf contains soil properties for selected STU's and for different soil horizons. For that reason Est_hor.dbf is recommended to be the primary data source for soil parameters that are used in leaching simulations.

Although a number of hydrologic pedotransfer functions exist, HYPRES pedotransfer functions were however explicitly tailored to the data structure and texture classification in the European Soil Map. Therefore preference should be given to HYPRES when deriving hydrological parameters.

Data distribution

The European Soil Map is available in Arc/Info format and is distributed by the European Soil Bureau:

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For information on SPADE-2 contact:

Office for Official Publications of the European Communities

2, rue Mercier

L-2985 Luxembourg

Tel: (352) 2929-1

Email:info@publications.europa.eu

http://publications.europa.eu/

Documentation

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Nemes A., Wösten J.H.M., Lilly A., and J. H. Oude Voshaar. 1999. Evaluation of different procedures to interpolate particle-size distributions to achieve compatibility within soil databases. Geoderma 90:187-202.

European Groundwater Map

General description

In 1982 the European Commission published a set of 38 1 : 500,000 scale maps detailing ground water resources in 9 countries which formed the European Community before the accession of Greece in 1981 (CEC, 1982). This set of maps and reports is currently the most comprehensive compilation of consistent information on ground water resources in these 9 countries. The existing maps were digitized in an industry funded project (Hollis et al., 2002).

- EC Member States of 1977, UK, Ireland, Denmark, Germany (excluding former GDR), The Netherlands, Belgium, Luxemburg, France, Italy

Figure A8-3. Spatial Extent of the European Groundwater Map

Contents

The ground water map contains a set of different themes:
- An inventory of aquifers: Geographic extension, geological and lithological features, aquifer type (confined or unconfined) and flow characteristics (interstitial, fissured and karst)
- The hydrogeology of aquifers: Transmissivity and piezometry where available, direction of ground water flow, relationship with surface waters and between aquifers, occurrence of salt water intrusion
- Abstraction points for ground water

Types and extension of aquifers:

The type and properties of aquifers are described by three sets of information:
- The type of aquifer - unconfined, confined or complex;
- The nature of water movement - intergranular, fissure, mixed or karstic ;

- Special cases like alluvial aquifers

Relevance of types of aquifers to pesticide fate assessment:
- An *unconfined aquifer* can potentially receive recharge over the whole of its area, while a *confined aquifer* will tend to have a proportionally smaller recharge area, which will itself be unconfined; *Unconfined aquifers* may be vulnerable to pesticide leaching, dependent upon the nature of overlying deposits and the thickness of the unsaturated zone;
- *Confined aquifers* are afforded significant protection by the overlying confining bed (which is not depicted on the map).
- *complex aquifers*- studies in these areas would benefit from more detailed geological mapping in order to more accurately ascertain the extent and lithological heterogeneity of such aquifers.

Relevance of nature of water movement to pesticide fate assessment:
- *Intergranular flow*- water moves along tortuous flow paths, which provides both time and the potential for significant interaction with the aquifer matrix;
- *Fissure flow*- fractures and fissures allow for fast flow rates with limited contact with aquifer media. The aquifer matrix may be calcareous or non-calcareous. Localised karst flow may occur in some portions of the aquifer;
- *Mixed*- the combination of the characteristics of both intergranular and fissure flow allows for fast flow rates together with a large intergranular storage, into which pollutants may diffuse from the fissures. While flow will be dominantly through the fissures, the ground water resource comes mainly from ground water released from intergranular storage by falling ground water levels.
- *Karst flow*- the large solution channels associated with karstic terrain allow for very fast flow rates (of the order of kilometres per day) with limited contact with aquifer media, but probably in a high pH environment.
- *Karst flow*- rates can be high enough to generate turbulent flow, allowing the movement of particulate and colloidal material through the ground water system.
- Normal unconfined *karstic aquifers* are often associated with a karst terrain, characterized by solution channels, closed depressions, sinkholes and caves. These allow very rapid movement of surface water and recharge in to the ground water system. Karst aquifers can be very vulnerable to pollutants entering from the surface water system.

The relevance of special cases like alluvial aquifers to pesticide fate assessments:

- *Alluvial aquifers* are disproportionately important for water supply purposes; and are potentially vulnerable to contamination from the induced infiltration of contaminated surface water

Ground water hydrogeology data

Information on ground water flow is only partly provided in the map. Risks assessments of regional ground water exposure to pesticides would benefit from more detailed information on flow directions. The respective data could be used to assess (1) contaminant flow from potential vulnerable areas from where pesticide entries might occur and (2) potential exposure of vulnerable receptors like wetlands or springs. The current data set however does not allow for such detailed assessments on the whole study area.

Also contour lines are given only for parts of the European Groundwater Map. More detailed information on the topography of aquifers and a high resolution digital elevation model would allow for the estimation of depths of ground water tables which is an important input parameter in leaching models. Currently this information cannot be derived with the required accuracy based on the existing map.

Areas of saltwater intrusion indicate aquifers that are unlikely to be used as source for drinking water.

Ground water abstraction data

The size of abstraction from wells or springs provides information about the likely size of its source area and the importance for local water supply. Mine drainage is a special case of ground water abstraction, indicating a significant human alteration of ground water flow.

General considerations for environmental risk assessments of pesticides

The European Groundwater Map is currently the most comprehensive data set on ground water resources in Europe. Pesticide risk assessments on a regional scale would benefit from further work in the area of hydrogeology and in particular of an extension of the ground water map to additional member states. This probably will be achieved soon within the framework of the implementation of the water framework directive. At present the most important use of the European Groundwater Map is the identification of aquifer locations and the potential exclusion of areas without any significant ground water resources from leaching assessments. In turn regional leaching assessments could be targeted to areas of concern based on the presence of vulnerable aquifers that are significant sources for drinking water.

Data distribution

The digitized version of the Groundwater Resources Map of Europe is available in ArcView 3.2 (shape file) format. The distribution of the data will be through the Office for Official Publications of the European Communities in Luxembourg.

Documentation

CEC. 1982. Groundwater resources of the European Community: Synthetical Report. Commission of the European Communities, Directorate-General for the environment, consumer protection and nuclear safety. Th. Schäfer GmbH, Hannover. 75 pp.

Jones R.J.A., Hollis J.M. L. Montanarella and S.K. Selvaradjou (2004): Groundwater Resources of Europe. Maps at 1 : 500,00 scale & GIS database [CD-ROM]. EUR 7940 EN. 4 September 2004.

Further information on these maps can be obtained through:

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IPCC Global Climate Data

General description

The Intergovernmental Panel on Climate Change (IPCC) has been established by the United Nations Environment Program (UNEP) and the Word Meteorological Organisation to assess global climate change phenomena. The IPCC distributes global climate data as monthly series from 1960 to 1990.

- All continents except Antarctica

Figure A8-4. Spatial extent of the IPCC global climate data base

Contents

The IPCC global climate data set consists of a multi-variate 0.5º latitude by 0.5 º longitude resolution mean monthly climatology for global land areas, excluding Antarctica, constrained to the period 1961-1990, together with monthly time series at the same resolution for the period 1901-1995. The mean 1961-1990 climatology comprises a suite of eleven surface variables: precipitation (PRE) and wet-day frequency (WET); mean, maximum and minimum temperature (TMP, TMX, TMN); diurnal temperature range (DTR); vapour pressure (VAP;) global radiation (RAD;) cloud cover (CLD); frost frequency (FRS); and wind speed (WND). There are additional datasets about climate anomalies in the same resolution. The anomaly time series component comprises all variables except global radiation and wind speed.

General considerations for environmental risk assessments of pesticides

The IPCC global climate data base contains monthly mean values for a 30 year period and is therefore best suited for long-term assessments of regional climate patterns and potential impact on leaching and degradation behaviour of active ingredients. The data base is however not appropriate to extract weather files for leaching models since it does not provide daily weather series.

Data distribution

The IPCC global data is available free of charge as zipped ASCII files from [http://ipcc-ddc.cru.uea.ac.uk/asres/baseline/climate_download.html]

Documentation

A detailed documentation of the IPCC global climate data was prepared by the University of East Anglia and can be accessed via [http://ipcc-ddc.cru.uea.ac.uk/cru_data/examine/cru_climate.html]

Digital Elevation Model

General description

In February of 2000 space shuttle *Endeavour* conducted an eleven-day mission to create the most complete topographic map of the Earth to date. The Shuttle Radar Topography Mission (SRTM) was an international project involving the United States Department of Defence National Imagery and Mapping Agency (NIMA), the National Aeronautic and Space Administration (NASA), the German Aerospace Centre (DLR), Dornier Satellitensysteme Germany, and the Italian Space Agency (ASI) and the Jet Propulsion Laboratory (JPL) at the California Institute of Technology.

Spatial extension

The experimental C-band and X-band interferometric synthetic aperture radar systems mapped over 80% of the Earth's surface between 60 degrees north and 56 degrees south latitude.

- All continents between 60 °North and 56 °Southern Latitude

Figure A8-5. Spatial extent of the Digital Elevation Model

Contents

NIMA will produce two public data sets, DTED-1 with worldwide coverage and DTED-2 for the US. Digital Terrain Elevation Data (DTED) sets consist of a uniform grid of latitude, longitude, and elevation data. DTED-1 grid posts are spaced at three arc second intervals (approx. 100m) and DTED-2 grid posts are spaced at one arc second intervals (approx. 30m). A third reduced resolution data set, DTED-0, was also produced for the globe having grid post spacing of 30 arc seconds (approx. 1km).

General considerations for environmental risk assessments of pesticides

In general digital elevation models have only a limited range of applications in leaching modelling studies. Nevertheless the data is of use for a more detailed assessment of landscape factors on a local or regional scale such as occurrence of slopes with limited potential of showing chromatographic vertical solute fluxes. Digital elevation models can also be used to assess the occurrence of certain soil types. Currently the delineation of certain soil polygons in the EU soil map is corrected on the basis of SRTM data since in some cases the boundaries of e.g. Fluvisols does not match the boundaries of floodplains.

Data distribution

SRTM data can be obtained from the United States Geological Survey (USGS) Data Center [http://srtm.usgs.gov/]. This server stores areas of up to 30°square (1.6 gigabyte/100 megabyte files) as downloadable data sets at no charge and areas of greater than or less than 30 degrees square on CDs at a cost of $32 per CD (approximately 600 megabyte each) plus a $45 processing and a $5 shipping charge. Available formats include ArcGrid, BIL, and TIFF

Documentation

A detailed documentation on SRTM data is available from National Aeronautic and Space Administration (NASA) and European Space Agency (ESA) websites:

- http://www2.jpl.nasa.gov/srtm/
- http://www.spaceflight.esa.int/file.cfm?filename=sts99obj

Administrative Boundaries (AD)

Description

NUTS version 7 (1999)
Boundaries of 1 328 NUTS regions (Nomenclature of Territorial Units for Statistics)
4 hierarchical levels
Resolution Scale: 1/1 000 000 (1000 €)
                       1/3 000 000 (700 €)

Spatial extent

National boundaries of all European countries are included
(EU-15, EFTA-4, AC-12)

Content

The Nomenclature of Territorial Units for Statistics (NUTS) was established by Eurostat more than 25 years ago in order to provide a single uniform breakdown of territorial units for the production of regional statistics for the European Union.

Since this is a hierarchical classification, the NUTS subdivides each member state into a whole number of NUTS 1 regions, each of which is in turn subdivided into a whole number of NUTS 2 regions and so on.

At the regional level (without taking the municipalities into account), the administrative structure of the member states generally comprises two main regional levels (Länder and Kreise in Germany, régions and départements in France, Comunidades autonomas and provincias in Spain, regioni and provincie in Italy, etc.).

The grouping together of comparable units at each NUTS level involves establishing, for each member state, an additional regional level to the two main levels referred to above. This additional level therefore corresponds to a less important or even non-existent administrative structure, and its classification level varies within the first 3 levels of the NUTS, depending entirely on the Member State: NUTS 1 for France, Italy, Greece, and Spain, NUTS 2 for Germany, NUTS 3 for Belgium, etc.

Some examples for the definition of NUTS in different countries are summarised in Table A8-3.

Table A8-3. Example NUTS levels in the different Member States of the EU

Country	NUTS 1	NUTS 2	NUTS 3
Österreich	Südösterreich	Kärnten	Klagenfurth-Villach
Belgique	Vlaams Gewest	Provincie Limburg	Hasselt
Deutschland	Bayern	Oberbayern	München
Danmark	Danmark	Danmark	Ribe amt
Expaña	Este	Cataluña	Barcelona
France	Bassin Parisien	Bourgogne	Nièvre
Italia	Centro	Toscana	Pisa
Nederland	Noord-Nederland	Friesland	Noord-Friesland
Luxembourg	Luxembourg	Luxembourg	Luxembourg
Portugal	Continente	Norte	Ave
Sverige	Sverige	Östra Mellansverige	Uppsala län
United Kingdom	North West	Greater Manchester	Greater Manchester South

A detailed overview about the resolution in the different countries is summarised in http://europa.eu.int/comm/eurostat/ramon/nuts/codelist_en.cfm?list=nuts

Data distribution:

Data can be ordered via one of the EUROSTAT Data shops.-

      Resolution Scale: 1/1 000 000 (1000 €)

                             1/3 000 000 (700 €)

Documentation:

More information on the NUTS can be found at:

      http://europa.eu.int/comm/eurostat/ramon/nuts/home_regions_en.html

European Zonal Map

Description

The new Regulation for the Placement of Plant Protection Products on the Market provides for a system of mutual recognition in zones (North-Central-South). The zones are listed in Annex 1 of the regulation. The European Zonal Map listed below has been created on the basis of this appendix.
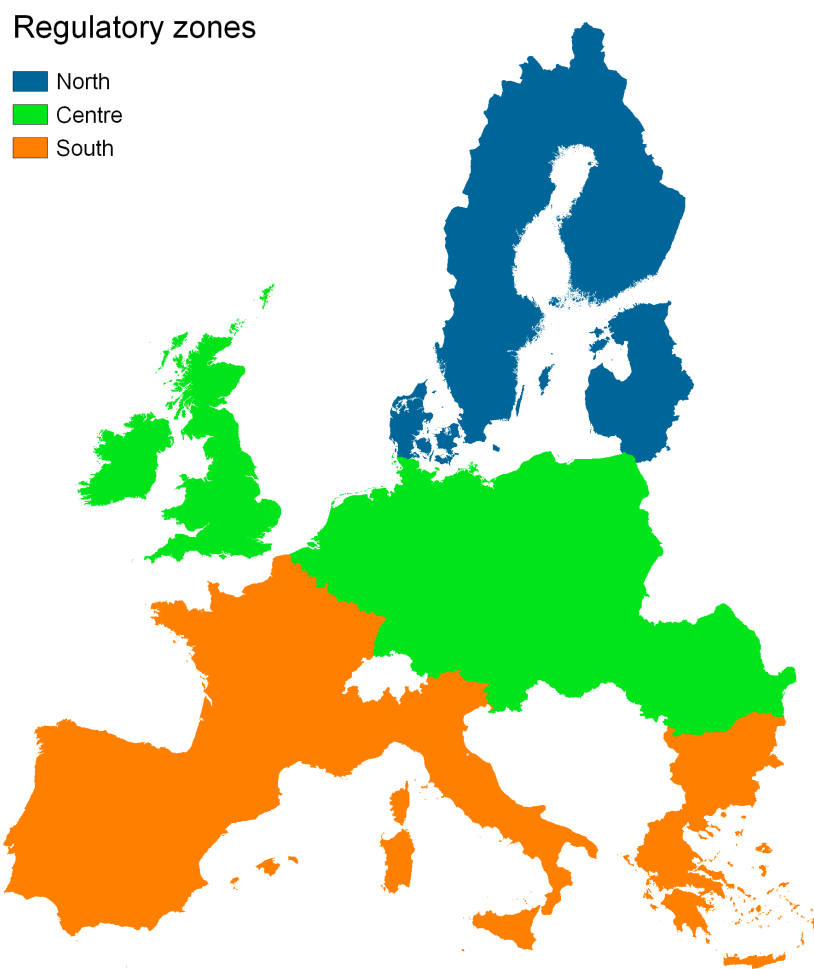
Figure A8-6. Proposed zonal map of Europe.

European Census Data (AD)

Description

New CRONOS: long-term series data (monthly, quarterly, yearly) on the nine themes of the official European statistics. A demo CD-ROM is available.

Spatial extent

National boundaries of all European member states are included.

Content

Data are available for in total 9 categories (general statistics, economy and finance, population and social conditions, industry, trade and services, agriculture and fisheries, external trade, transport, environment and energy, science and technology). The data are provided in extended tables based on a hierarchical structure (categories, domains, collections, tables).

In the category "Agricultural and Fisheries" in total 11 domains are considered. Most interesting for FOCUS will be the collection PROD_VEG ("crop products") in the domain ZPA1 (Agricultural Products). The collection contains two data fields ("Fruits and vegetables" and "Crops products (excluding fruits and vegetables)". The data are provided with an annual resolution. Data are available for more than 200 crops.

This high resolution of crops is provided only on the member state level, when this data is purchased from the Eurostat-data-shops. Data on the regional level (NUTS 1 and 2) is available but only for a following crops:

- cereals (including rice)
- cereals (without rice)
- common wheat and spelt
- durum wheat
- winter wheat
- rye
- barley
- grain maize
- rice
- potatoes
- legumes
- sugar beets
- oilseeds
- rape - turnip rape

- sunflower seed
- soybean
- oil flax
- cotton
- tobacco
- orchards
- olives

There are data gaps for some combinations of crops and member states.

Data distribution:

Data can be ordered via one of the EUROSTAT Data shops. Resolution Scale: resolution 21 crops listed, regional level (NUTS 1, 2, 3): costs about 130 Euro (for one year)

Documentation:

More information on the CRONOS Data base can be found at:

http://www.eu-datashop.de/datenba/EN/allgem/infoda_1.htm

MARS Climate Data Base

Description

Joint Research Centre (JRC) at Ispra, Italy, holds long-term weather data compiled as part of the Monitoring Agriculture by Remote Sensing (MARS) project. The data were derived using a method developed at the former Staring Centre (now Alterra). The MARS data base contains daily meteorological data spatially interpolated on 50 x 50 km^2 grid cells. The original weather data originate from approximately 1500 weather stations across Europe, Maghreb countries, and Turkey, and are based on daily data for the period 1971 to date, which was purchased from various national weather services. Some of the data were obtained from the national meteorological services under special copyright and agreements for MARS internal use only, so that data at station level are not available, only interpolated daily weather data are available.

In the MARS data base, the basis for the interpolation is the selection of the suitable combination of weather stations for the determination of the representative meteorological conditions for a grid cell. The selection procedure relies on the similarity of the station and the grid centre. This similarity is expressed as the results of a scoring algorithm that takes the following characteristics into account:

- Distance

- Difference in altitude

- Difference in distance to the coast

- Climatic barrier separation.

Spatial extent

All 25 EU countries are included. Figure A8-7 shows an example of weather information obtained from this data base.
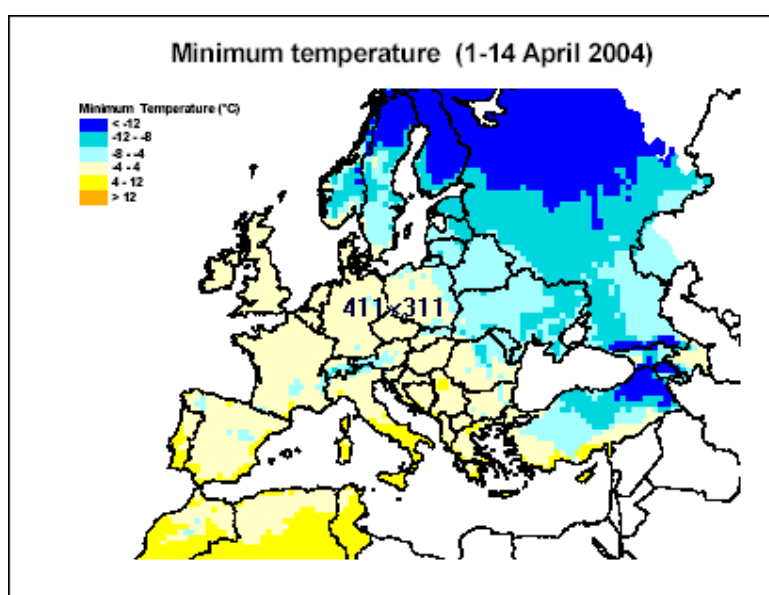
Figure A8-7. An example of weather data obtained from the Mars data base.

Content

The following parameters are available:

- Date
- Minimum air temperature
- Maximum air temperature
- Precipitation
- Wind speed
- Deficit vapour pressure
- Calculated potential evaporation (Penman-Monteith adopted FAO approach)
- Calculated global radiation according to Angströms equation, which is sunshine hours based.

Data distribution:

The current version of the MARS weather data base is distributed by the MARS unit of JRC, who are cooperating with Alterra and Meteo Consult (a private meteo company in the Netherlands). Whether the weather data can be distributed free of charge is not clear since conditions of JRC state that further distribution is not allowed.

Documentation:

More information on MARS weather can be found at:

> ftp://mars.jrc.it/Public/CGMS/doc/GridWeather.doc (login anonymous with your e-mail address as password)

Irrigation Data Base

Description

A digital map of irrigated areas is available as a raster map with resolution of 0.5^o latitude by 0.5^o longitude. For the whole land area of the globe (except Antarctica), the data set provides the irrigation density around 1995, i.e. the percentage of each grid-cell equipped for controlled irrigation in the 1990s. The areas for irrigation include:

- areas with full or partial controlled irrigation
- spate irrigation areas
- equipped wetlands and inland valley bottoms.

The irrigation areas do not include cultivated wetlands and flood recession cropping areas. The area actually irrigated was smaller than the area that was equipped for irrigation, but the area actually irrigated is unknown for most countries. Therefore, note that the map presents the area *equipped for irrigation* rather than the area irrigated. A full description is given by Siebert and Döll (2001).

Spatial extent

The whole world, so the all 25 EU countries are is included.

Figure A8-8 shows a map generated from the data base.
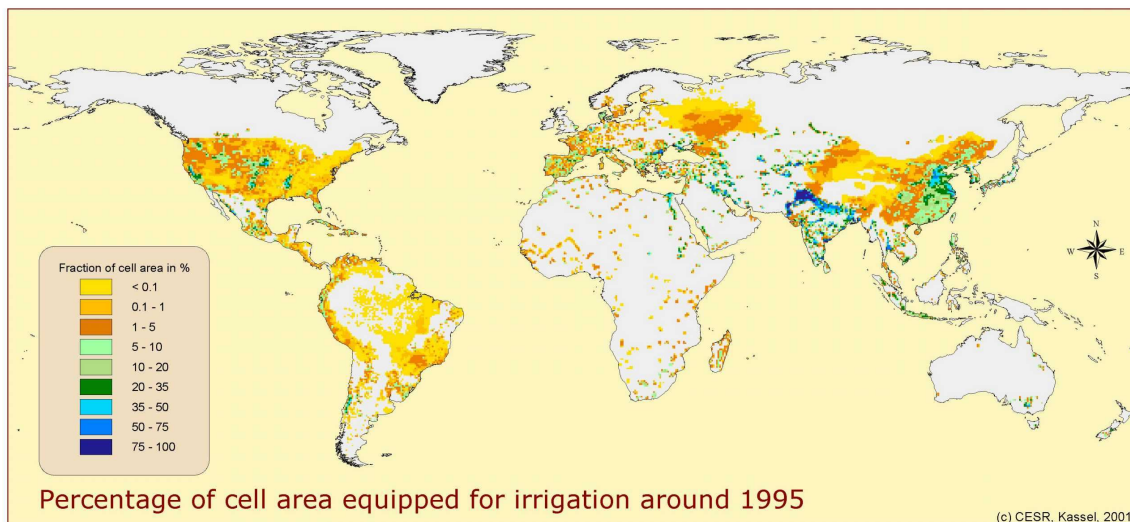
Figure A8-8. Percent of land equipped for irrigation.

Figure A8-9 shows the percentage of the area equipped for irrigation within Europe. This map was created for EuroPEARL by converting the original map to a different projection and grid cell size of 25x25 km^2. New member states are not included.
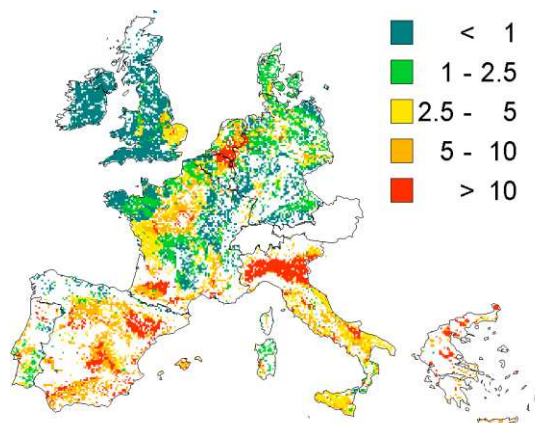
Figure A8-9. Percent of land equipped for irrigation.

Content

- Fraction of the grid cell equipped for irrigation

Distribution

The map was made available for use within the APECOP project.

Documentation

Siebert, S. and P. Döll. 2001. A Digital Global Map of Irrigated Areas – An update for Latin America and Europe. Report A0102, Centre for Environmental Systems Research, University of Kassel, Germany.

The Map of Organic Carbon in Topsoils in Europe

General Information

In 2004 the European Soil Bureau published a digital map (1 x 1 km raster) of organic carbon contents in topsoils. The map was compiled by means of transfer functions that considered soil properties as represented by the European Soil Map, information on land use as given by CORINE Land Cover and temperature data. A detailed description of the methodology is given in Jones et al. (2004, 2005). The authors did not consider the moisture status of soils when compiling the map because the influence of moisture is implicitly taken into account with the inclusion of the soil type (parameter SOIL) in the soil mapping unit (Jones et al, 2004, 2005). The influence of temperature on organic carbon contents was taken into account in accordance with the principle that organic matter contents increase when annual average temperatures are decreasing.

Calculated contents of organic carbon were compared with measured data from soil surveys in the U.K (5500 data points) and Italy (6800 data points). The comparison of calculated OC and measured OC revealed a statistically significant match between measured and simulated data in both sampling regions.

Figure A8-10. Spatial extent of the map of organic carbon contents in Europe

Documentation

Jones, R. J. A., R. Hiederer, E. Rusco, and L. Montanarella. 2005. Estimating organic carbon in the soils of Europe for policy support. European Journal of Soil Science, 56(5):655-671.

Jones, R.J.A., R. Hiederer, E. Rusco, P. J. Loveland, and L. Montanarella. 2004. The map of organic carbon in topsoils in Europe, Version 1.2, September 2003: Explanation of Special Publication Ispra 2004 No.72 (S.P.I.04.72). European Soil Bureau Research Report No.17, EUR 21209 EN, 26pp. and 1 map in ISO B1 format. Office for Official Publications of the European Communities, Luxembourg.

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http://publications.europa.eu/

APPENDIX 9. COMPARISON OF THE METAPEARL AND INDEX METHOD FOR HIGHER TIER SPATIAL MODELLING

As described in Section 7.2.5, the work group refers to two methods for calculating ground water vulnerability. In the first method (Appendix 4), referred to as the index method, attribute data are combined in simple arithmetic rules to yield a vulnerability index. Weights are assigned to the attributes in terms of the sensitivities of individual parameters to leaching. The second method is based on a metamodel of EuroPEARL (Appendix 5). The method is referred to as the MetaPEARL approach. Both methods generate spatial maps of candidate scenarios meeting the predefined vulnerability concept. Candidate scenarios are subsequently parameterised before higher tier leaching assessments are made using the standardised FOCUS models.

Both approaches may yield different spatial maps of candidate scenarios, which subsequently may impact the ground water assessments. Considering the strategy to develop harmonised procedures, elucidating and documenting potential differences is necessary. The objectives of this section are therefore:

   i)   to compare assessments made by the two present approaches for two contrasting case studies (a data rich and a data poor environment)
   ii) to analyse the strengths and weaknesses of both methods

Comparison of two spatial methods to define candidate scenarios

Materials and methods

The comparison is done using two data sets:

   * A regional assessment in a data poor environment. The case study is implemented for assessing a sugar beet cropping scenario in northern France. See Appendix 4 for more details.
   * A national assessment in a data rich environment. For this case study, a reference model (GeoPEARL) is available. The case study is implemented for the Netherlands. The data set is described in the GeoPEARL manual and available with the model and some details are given in Appendix 5.

The most important difference between the two data sets is that in the first case there are not sufficient data available to parameterize a fully spatially-distributed model like GeoPEARL. In

the second case, a spatially-distributed model is available, which can serve as a reference (because the spatially distributed model is a normal FOCUS leaching model – see Appendix 5). To avoid possible bias due to the use of different data sets, the two methods were applied to exactly the same data set (same resolution, projection).

The northern France data set contained almost everything to run both the index and MetaPEARL. Water content at field capacity was missing in the data set – this parameter was obtained from the 1:1.000.000 soil map using the normal procedures (conversion of textural class to water content at field capacity using the Hypres rules). Organic carbon of the topsoil was converted to organic carbon of the upper meter, assuming a zero content for the 30-100 cm soil layer (worst case – see also Appendix 5).

Results

Case study 1: Assessment in data poor environment: Assessing a sugar beet cropping scenario in northern France

Figure A9-1 shows the most important spatially distributed model inputs for MetaPEARL and the index method, i.e. rainfall, temperature and organic matter. Based on the weather data, climatic zone II (temperate and dry) was chosen for the MetaPEARL application.

Annual rainfall (m year^{-1})   Mean annual temperature (deg C)   Organic matter content (%)

< 0.6	
0.6 - 0.7	
0.7 - 0.8	
0.8 - 0.9	
> 0.9	

< 10	
10 - 11	
11 - 12	
> 12	

< 0.01	
0.01 - 0.02	
0.02 - 0.03	
> 0.03	
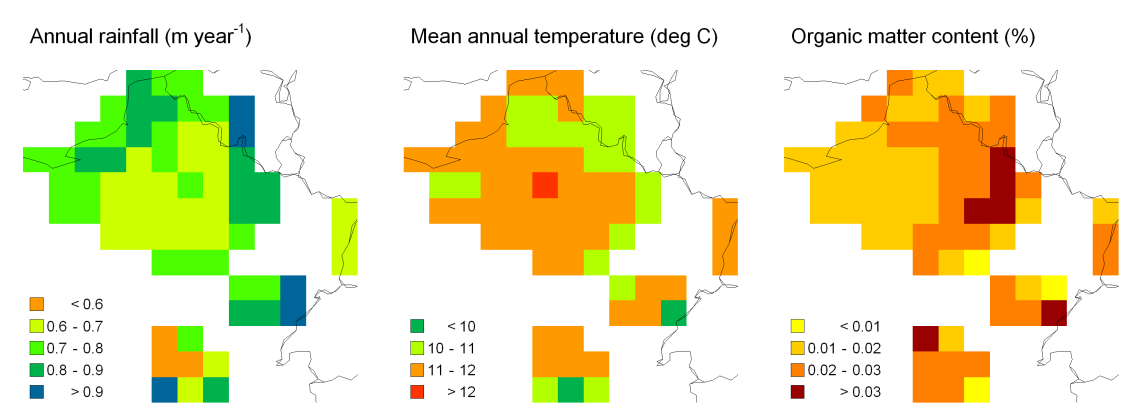
Figure A9-1. Basic data in the northern France data set.

Table A9-1 shows the weighting factors for the index method, as determined with Equation A4-2. (see also Appendix 4, Table A4-4).

Table A9-1. Weighting factors for the index method.

	A	B	D
Châteaudun			
P	0.52	0.72	0.62
T	0.09	0.06	0.08
OC	0.39	0.21	0.31
Piacenza			
P	0.38	0.70	0.53
T	0.10	0.06	0.07
OC	0.52	0.24	0.40
Average			
P	0.45	0.71	0.57
T	0.10	0.06	0.07
OC	0.45	0.23	0.35

The weighting factors are substance dependent: substance B shows a lower sensitivity to organic matter than substance A because the sorption coefficient is lower. However, there is a dependency on the selected scenario. Weighting factors based on the Châteaudun scenario show more sensitivity to rainfall than weighting factors based on Piacenza. This is probably one of the most critical issues in the application of the index method – the weighting factors are based on scenarios that are not part of the landscape to be evaluated.

Maps generated by MetaPEARL and the index method for the three FOCUS substances A, B and D are shown in Figure A9-2.
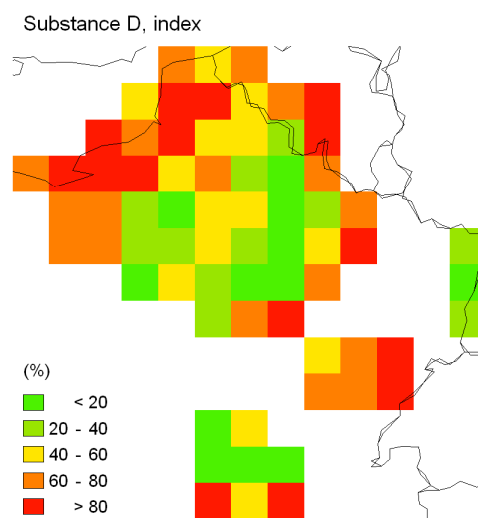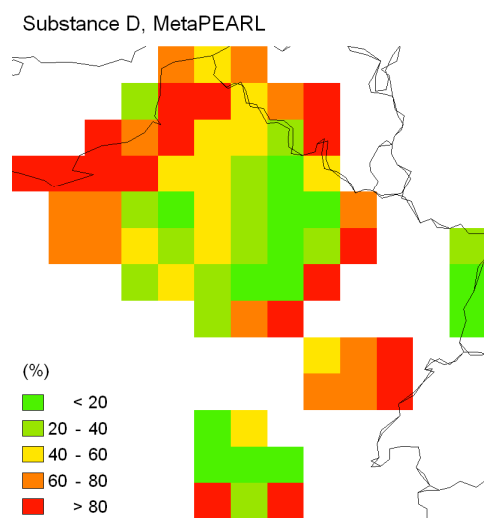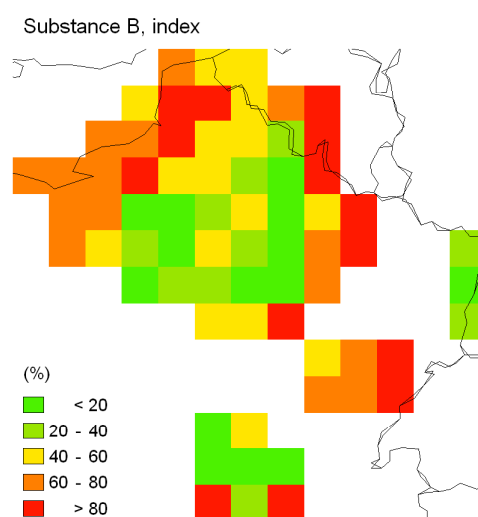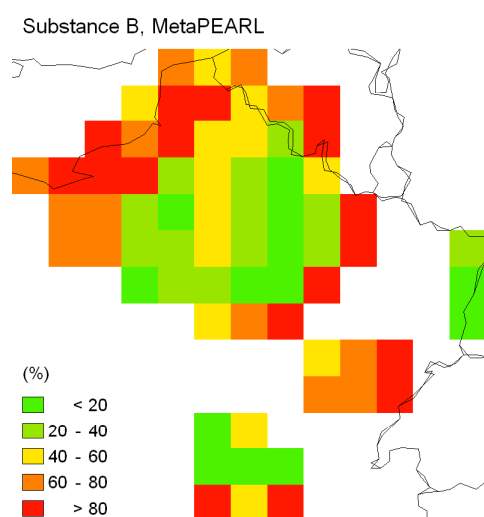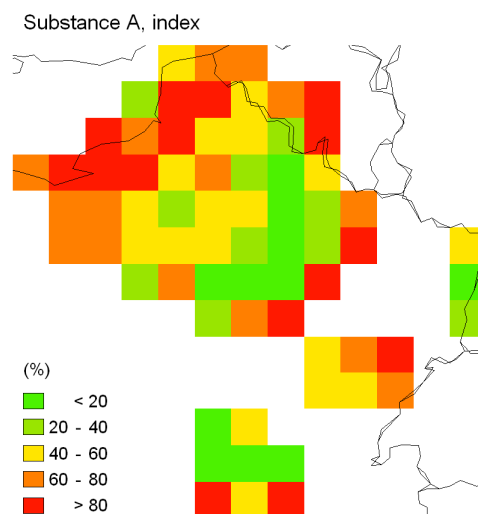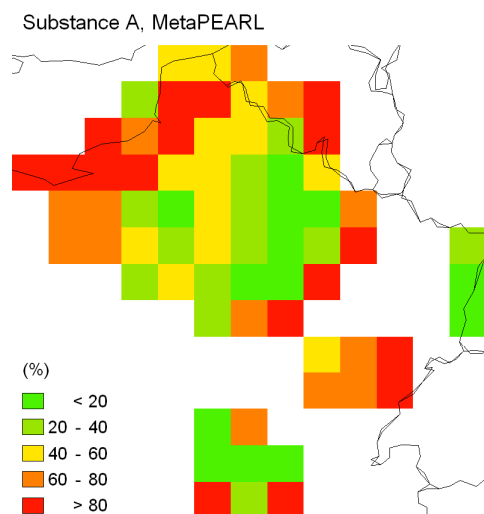
Figure A9-2. Ground water vulnerability for FOCUS substance A, B and D as predicted by MetaPEARL and the index method.

Figure A9-3 shows the differences between the maps generated by both methods. Figure A9-4 shows a frequency distribution of the differences.

Comparison of MetaPEARL and the revised Index for the Northern France case
$Vulnerability_{MetaPEARL} - Vulnerability_{Index}$
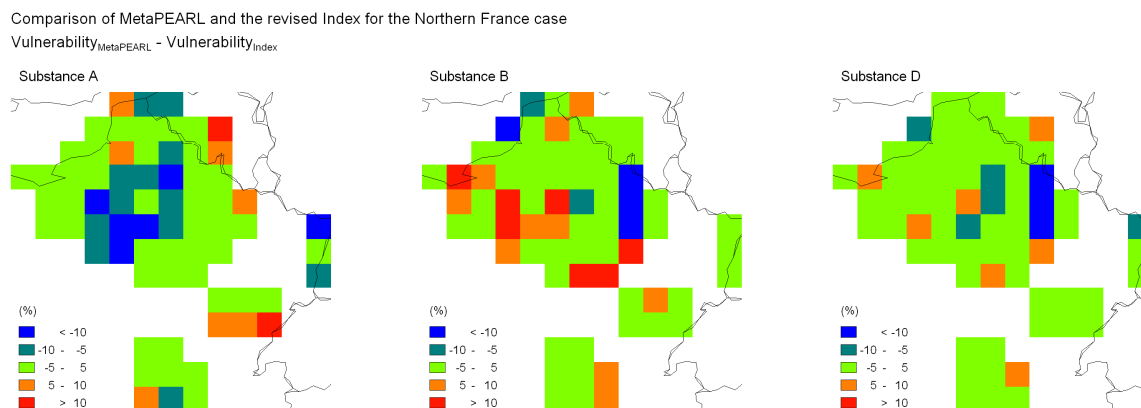
Figure A9-3. Difference between the maps generated by MetaPEARL and the index method.

Frequency distribution of the differences between MetaPEARL and the Index
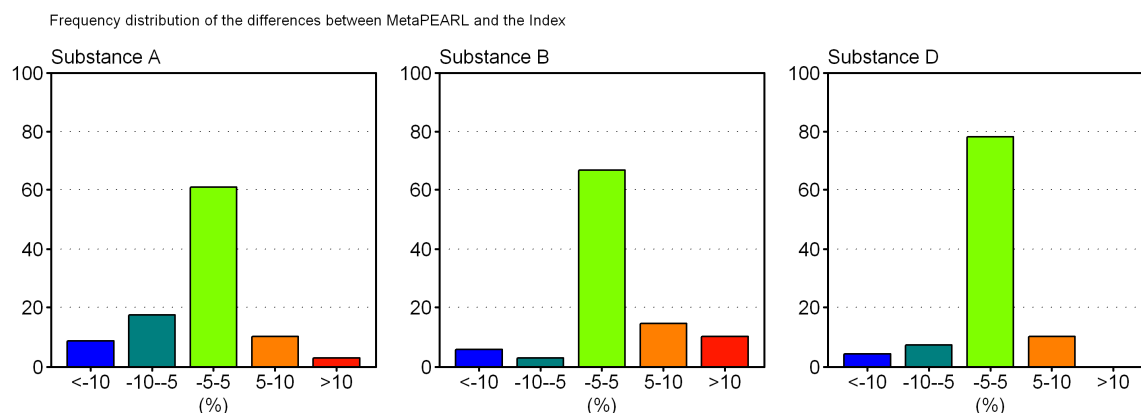
Figure A9-4. Frequency distribution of the maps shown in Figure A9-3.

Figure A9-4 shows that for all three substances, more than 60% of the cells do not differ more than 5%. Only 5-18% of the total number of grid cells differ more than 10%. This implies that the correspondence between the two methods is rather good.

According to the suggested protocol in Section 7.2.5, a series of grid cells should be selected in the 80-90% vulnerability range. This is done for the three FOCUS substances. Results shown in Figure A9-5 demonstrate that there is an overlap between the selected grid cells. There are, however, also differences.

Substance A, MetaPEARL

Substance A, Index

(%)
☐ < 80
🟧 80 - 90
☐ > 90

(%)
☐ < 80
🟧 80 - 90
☐ > 90

Substance B, MetaPEARL

Substance B, Index

(%)
☐ < 80
🟧 80 - 90
☐ > 90

(%)
☐ < 80
🟧 80 - 90
☐ > 90

Substance D, MetaPEARL

Substance D, Index

(%)
☐ < 80
🟧 80 - 90
☐ > 90

(%)
☐ < 80
🟧 80 - 90
☐ > 90
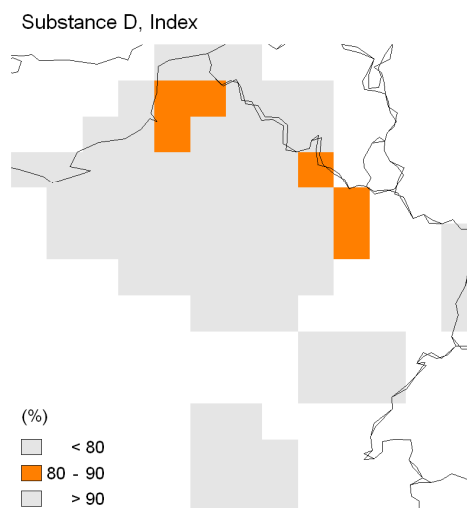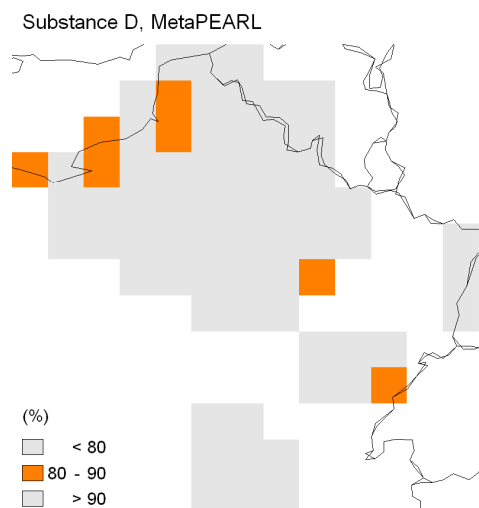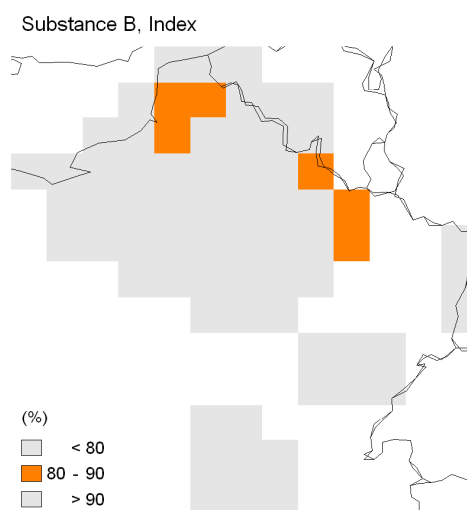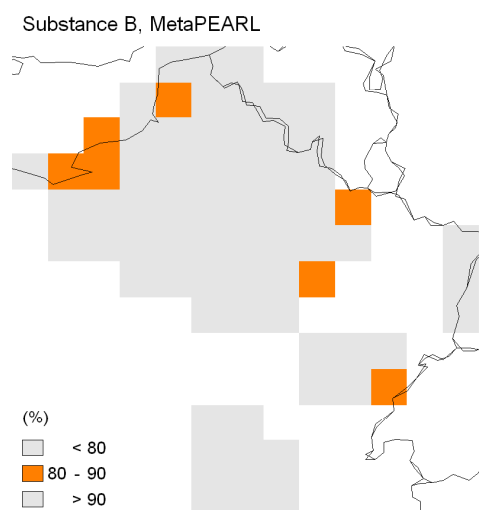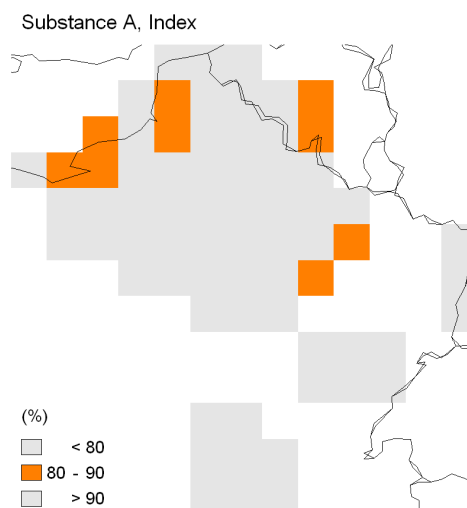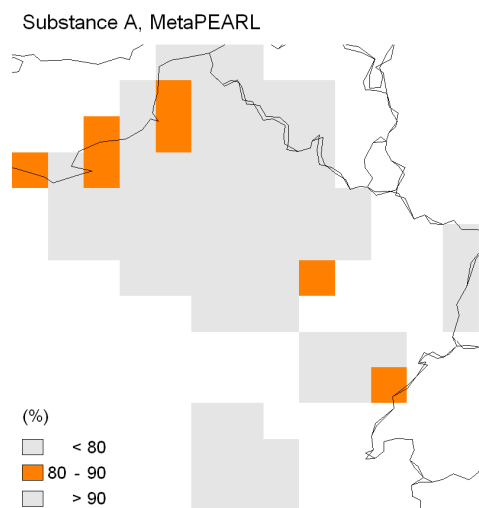
Figure A9-5. Candidate scenario grid for FOCUS substances A, B and D as selected with MetaPEARL (left) and the index method (right).

Case study 2: Assessment in data rich environment: National assessment in the Netherlands

The analysis for the index method started with the derivation of the weighting factors. In the Netherlands, the FOCUS Kremsmünster scenarios are applied as the first tier in pesticide registration. For this reason, the Kremsmünster scenarios were used to obtain the model sensitivities. The analysis was done for FOCUS substance A, B and D. A summary of results is shown in Table A9-2. The analysis below shows that organic matter has a higher weighting factor compared to the northern France case which follows from the fact that the climatic variation is small in the Netherlands.

Table A9-2. Summary of maximum ratios of variance (ROV) and resulting weighting factors for rainfall, temperature, and organic matter content in the topsoil.

Factor	A	B	D
Winter rainfall	0.25	0.11	0.09
Temperature	0.07	0.15	0.05
Organic matter	0.68	0.74	0.86

The weights in Table A9-2 were used to generate the ground water vulnerability maps with the index method. Results are shown in Figure A9-6. Visual inspection of the maps shows that the correspondence between the reference model (GeoPEARL) on the one hand and the index / metamodel method on the other hand is good. This is confirmed by the correlation between the maps, as shown in Figure A9-7.

Groundwater vulnerability, substance A
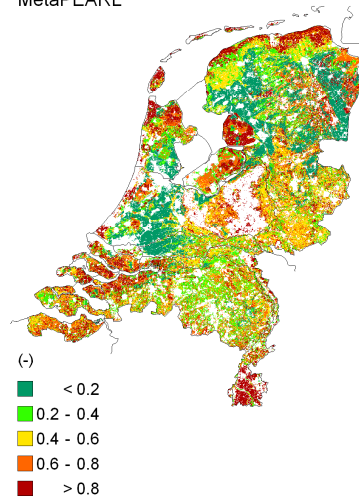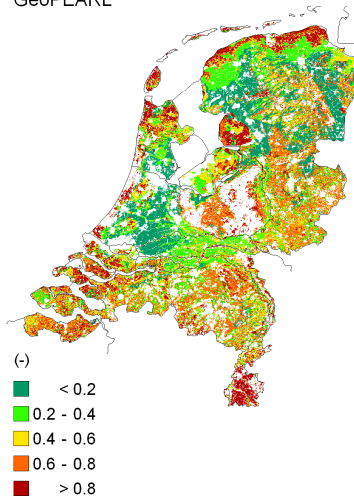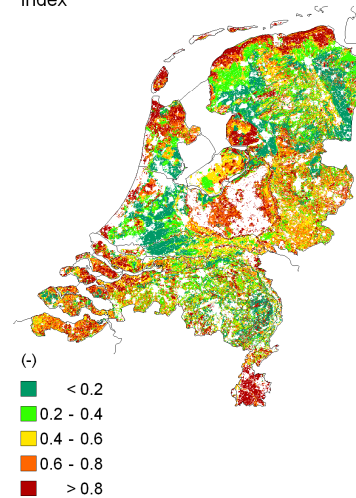
Groundwater vulnerability, substance B

Groundwater vulnerability, substance B
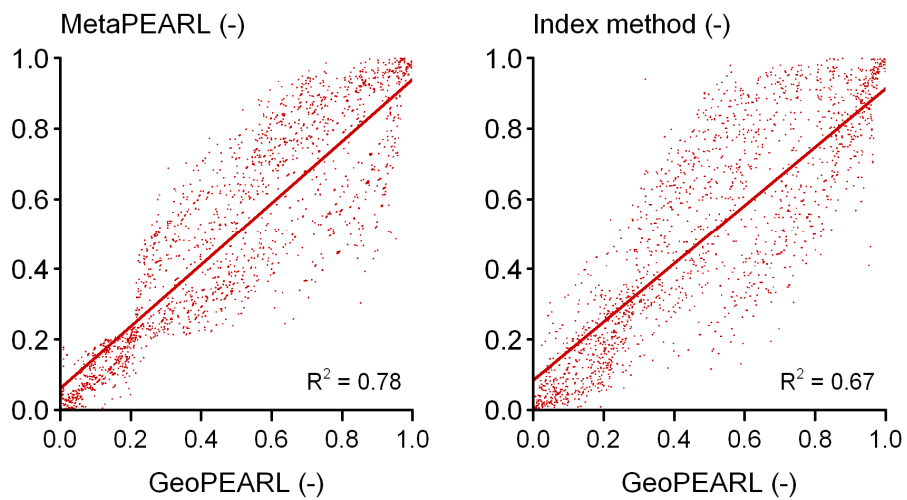
Figure A9-6. Ground water vulnerability predicted with GeoPEARL and with MetaPEARL and the index method.
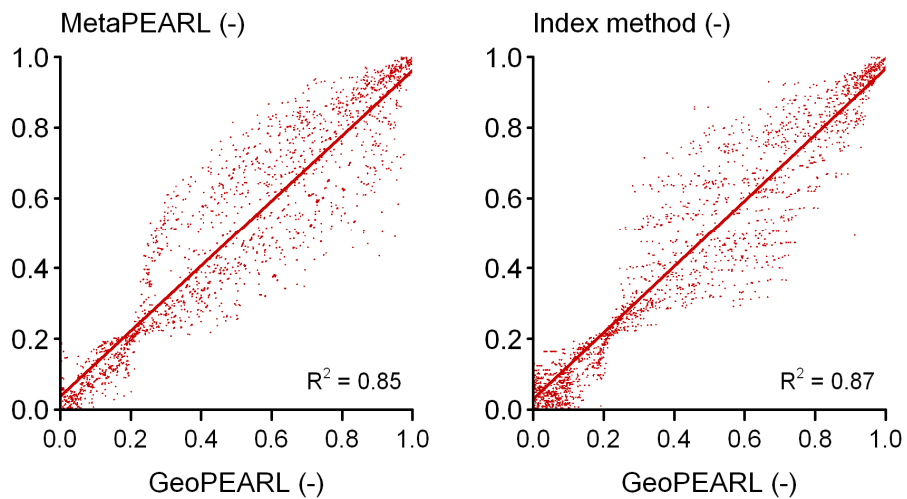
Figure A9-7. Ground water vulnerability predicted with GeoPEARL compared with ground water vulnerability predicted by MetaPEARL and the index method.

The three methods were used to select 26 use specific Tier 2b scenarios. The crops varied from major crops (maize and potatoes) to minor crop (legumes and cannabis). First, all plots in the 80-90th percentile vulnerability range were selected as candidate scenarios. Then the dominant plots were selected as the final Tier 2b scenario (see Appendix 5 for details). Results are shown in Figure A9-8. The figure shows that MetaPEARL method generally performs better than the index method (MetaPEARL is generally slightly above the 1:1 line, which was intended because Tier 2b scenarios must be more conservative than GeoPEARL). For substance A and substance B this can be explained from the correlation between the various vulnerability maps, as shown in Figure A9-7. For substance D, the lower performance of the index model is hard to explain since the correlation between the index model and GeoPEARL is almost the same as the correlation between the MetaPEARL method and GeoPEARL (Figure A9-7).

Comparison of scenarios selected with GeoPEARL, MetaPEARL and the Index method
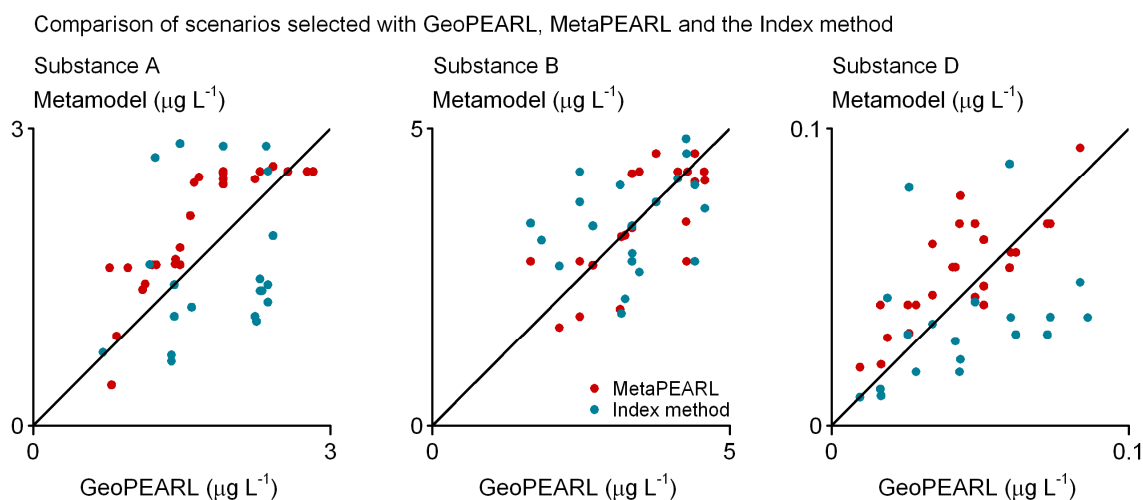
Figure A9-8. Tier 2b scenario calculations (selected ground water vulnerability maps predicted by MetaPEARL or the index method) as a function of Tier 3 calculations (simulated with GeoPEARL). The individual points are target concentrations for each of the 26 GeoPEARL crops.

Conclusions of the comparison, based on the two case studies

The work group refers to the index method (Appendix 4) and metamodel method (Appendix 5) for deriving Tier 2b scenarios. Both methods can be applied in data rich and data poor environments and therefore the application of either method to the intended use is feasible.

The spatial pattern of ground water vulnerability predicted by the two methods shows a strong correspondence.

In the data rich environment where a benchmark against a full spatially distributed model is possible, the spatial patterns of ground water vulnerability also compared well to the spatial pattern predicted by a benchmark model (i.e. GeoPEARL). The correlation is generally above 80% (with an exception for the index model and substance B).

For the case study in data poor environment (the French case), there was an overlap in the selected candidate scenarios (i.e. the grid cells in the 80-90th percentile range). There were also, however, different grid cells.

In the data rich environment case study (the Dutch case), 26 use specific scenarios were selected from the predicted ground water vulnerability maps. The method described in Appendix 5 was used for this purpose, i.e. the dominant scenario within the 80-90th percentile range was selected. Despite the fact that the dominant scenario was chosen, both methods yielded different scenarios in virtually all cases. The regulatory endpoint obtained with tier 2b scenarios based on MetaPEARL fit the tiered assessment scheme (i.e. they are slightly more conservative than the predictions by GeoPEARL). In the case of the index, there is more scatter – some scenarios underestimate the leaching while others overestimate the leaching.

Analysis of strengths and weaknesses of the index and metamodel method

The following criteria should be considered when selecting an appropriate spatially distributed method in higher tiers:

- The method should be effective, i.e. it should meet the preset objective (in this case, it should lead to a conservative estimate of the 80th percentile in space, considering the soil map unit and the rotation time as the support scale for defining the leaching event and this conservatism has to be proven.
- The method should be efficient, i.e. it should use available data in an elegant way and lead to a fast, conservative estimate of the percentile in space and should therefore be easy to use.
- The method should be transparent and documented.

A summary of the major strengths and weaknesses of both methods is given in the section below.

The work group could not reach a consensus on a single method to be used in Tier2b. Maintaining both methods to assess spatial leaching patterns reflects to some extent the conceptual uncertainty in current understanding of large scale leaching process. The disadvantage of maintaining both methods is less harmonization and additional uncertainty.

The additional uncertainty is by definition an additional burden in the regulatory decision making process.

The MetaPearl method

Strengths

- Logical rules for selecting vulnerable areas are based on known fate and transport processes since the conceptual FOCUS leaching model is underlying MetaPEARL. Hence the modelling approach is consistent with the modelling approach used at higher tiers and therefore based on current knowledge of the behaviour of system.
- The approach is compatible with data in pan-European data bases, and can therefore directly be implemented at the pan European scale.
- Application of the European MetaPEARL on the Dutch case study (Appendix 5) showed that the model performance may be scale invariant. It therefore could be used to extrapolate, at least within homogeneous climatic regions.
- The logical rule to combine spatially distributed soil-climate data into vulnerability is based on a large set of reference simulations, covering substantially the soil-climate data space in Europe.
- The method is fast and easy to implement.
- The sensitivities of the MetaPEARL to variation in pesticide (K_{om}, DegT50) and soil-climate (mean discharge, mean temperature) properties are similar to the sensitivities of the original model FOCUS PEARL model.
- The selection of scenarios based on the methodology was, for an illustrated case study in the Netherlands, more conservative than scenarios build on the spatially distributed mechanistic model. This fits perfectly within a tiered assessment scheme.

Weaknesses

- Validity cannot be demonstrated.
- MetaPEARL inherits all weaknesses of the reference model on which MetaPEARL is based.
- MetaPEARL needs calibration with a reference model. Calibration can be space variant and a new version of MetaPEARL may be needed for each cropping area.
- The calibration introduces additional uncertainty on the prediction. This uncertainty may however in some cases be very small, but substantially at low concentration levels. Particular problems have been identified in dry climates, characterized by large variability of hydrological fluxes. In such case, spatial patterns generated by the steady state meta-model deviates substantially from the dynamic model simulations. MetaPEARL should not be used to simulate the regulatory end-point.
- The calibration results may be biased if the spread of the data points along the regression line is not uniform or if outliers exist. The use of robust regression techniques however should minimize such a bias.
- MetaPEARL deviates substantially from the reference model if organic matter profiles are substantially different from the normal profiles found in arable soils (e.g. peat soils covered by marine clay in the Netherlands).

The index method

Strengths

- The approach is directly compatible with data in pan-European data base, and can therefore directly be implemented at the pan European scale.

- The method is fast and easy to implement.
- Winter rainfall, organic carbon and mean temperature are considered as major drivers of leaching; other factors which may drive vulnerability (soil moisture which depends also on soil texture, summer rainfall, bulk density, irrigation, time of application (spring or autumn) can be incorporated if appropriate. The method is completely flexible to incorporate landscape factors since it only ranks the occurrence probabilities.
- Different factors can be weighted in the logical rule. The weighting factors can be attributed based on expert judgement or sensitivity analysis.

Weaknesses

- Validity cannot be demonstrated.
- Identification of vulnerability due to soil, climate and crop is based on simplified leaching concept which simplifies the pesticide fate and transport processes, i.e. the vulnerability is expressed as a spatial query in an environmental data base, combining spatial attributes which contribute to possible leaching by means of a simplified logical rule. This logical rule may not reflect the processes such as they are considered in the FOCUS Tier 1 models. Hence, inconsistency with a spatial distributed benchmark model may appear.
- The method becomes less objective if expert judgment is used for attributing weighing factors in the logical rules.
- The sensitivity analysis is region specific, probably application or product specific and likely scale specific. The weighting factors will therefore be case specific. For the French and Dutch case study, the weighting factors were significantly different.
- As a corollary, the weighting factors have been obtained only from a limited range of simulations.
- Contributing factors are considered to be normally distributed. This hypothesis may be violated, in particular for organic matter. This assumption may have strong impacts, because the vulnerability assessment is based on the "tail" of the distributions (i.e. 80-percentile in space). These tails are affected strongly by the distribution, particularly in non-linear systems.
- In both of the example cases (northern France and the Netherlands) the normality hypothesis was violated. In the Dutch data set, the mean value for organic matter, for example, is 0.12 while the median value is only 0.02, suggesting an extremely skewed distribution (caused by peat soils).

APPENDIX 10. THE PRINCIPLES OF INVERSE MODELLING

M. Vanclooster

Components of an inverse model

The forward model

The forward model is the model which calculates system response in terms of output values. In this case, these are the standard FOCUS leaching models, which calculate time series of soil moisture, soil temperature, soil pesticide concentrations, soil moisture fluxes, soil heat fluxes, and soil pesticide fluxes for the boundary conditions corresponding to those of the experiment.

The objective function

The objective (or merit or goal) function is a measure of the agreement between the data and a model with a particular parameter set **p** (e.g. the DegT50 value that has been used). During an inversion, this objective function will be optimised (i.e. maximised or minimised, depending on the definition of the objective function).

The criterion usually used is the weighted least squares error function (WLSE) defined as:

$$\Phi(\mathbf{p}) = \frac{1}{\sigma^2} \sum_{i=1}^{N} \left[y_i - y^*(x_i, \mathbf{p}) \right]^2$$

or in matrix notation

$$\Phi(\mathbf{p}) = \left(\mathbf{y} - \mathbf{y}^* \right)^T \mathbf{V}^{-1} \left(\mathbf{y} - \mathbf{y}^* \right)$$

where y_i is the ith element of the measured dataset **y** (e.g. the pesticide concentrations in the leachate of a lysimeter) at x_i (e.g. the different time steps) for $i=1,…, N$; $y^*(x_i, \mathbf{p})$ is the ith modelled answer of the vector **y*** for x_i and parameter set **p**, σ^2 is the variance and **V** the covariance matrix of the measurement errors. In inverse modelling, the WLSE is minimised. The WLSE can be extended to cases for which each data point (x_i, y_i) has a different known standard deviation σ_i (heteroscedasticity):

$$\Phi(\mathbf{p}) = \sum_{i=1}^{N} \left[\frac{y_i - y^*(x_i, \mathbf{p})}{\sigma_i} \right]^2 \equiv \chi^2$$

which follows a Chi-square distribution. In practical applications, the WLSE is often applied considering the error variance as being equal to 1. However, such functions do not permit the derivation of statistically sound indicators of parameter uncertainty (Hollenbeck and Jensen, 1998). In addition, the location of the minimum may also be affected when multi-informative objective functions are formulated.

Another objective function is the likelihood function $L_y(\mathbf{p})$ which gives, as a function of the parameter vector $\mathbf{p}$, the conditional probability of observing the data $\mathbf{y}$. If measurement errors are independent, normally distributed, and homoscedastic, i.e., measurement errors have the same variance, it can be shown that the likelihood function $L_y(\mathbf{p})$, is related to the WLSE by (see, e.g., Press et al.,1992)

$$L_y(\mathbf{p}) = f\langle \mathbf{y}|\mathbf{p}\rangle \propto \exp(-0.5\Phi(\mathbf{p}))$$

where $f\langle \mathbf{y}|\mathbf{p}\rangle$ represents the probability of $\mathbf{y}$ given $\mathbf{p}$.

Therefore, minimizing WLSE is equivalent to maximizing $L_y(\mathbf{p})$.

The optimisation algorithm

A successful inversion method also needs an efficient and robust optimisation algorithm, which in the case of the WLSE minimizes the object function or in the case of Ly(p) maximises the object function. When few parameters have to be estimated and the data quality is high, then model parameters can be estimated using local search algorithms such as the gradient based Levenberg Marquardt method (Marquardt, 1963) or the simplex method, which are classically used in relatively simple non-linear regression problems. These algorithms are readily available in standard software packages.

The inherent topographical complexity of the non-linear multidimensional objective functions encountered when estimating pesticide fate and transport parameters from transient experiments limits very often the classical gradient based local search optimisation algorithms to converge to the optimal solution. To overcome this, more efficient and reliable

global search optimisation algorithms have been proposed. Examples of global search algorithms are given in Table A10-1.

Table A10-1. Optimisation algorithms that have been used in soil transport modeling. Global search algorithms are recommended to get over the complex topography of the objective functions usually encountered in soil hydrology inverse problems.

Algorithm	Type	Reference
Levenberg-Marquardt	Local	Marquardt, 1963
Gauss-Newton	Local	
Nelder-Mead simplex (downhill simplex)	Local	Nelder and Mead, 1965
Sequential uncertainty domain parameter fitting	Global	Abbaspour et al., 1997
Simulated annealing	Global	Ingber, 1996
Annealing-simplex	Global	Pan and Wu, 1998
Genetic	Global	Vrugt et al., 2002
Shuffled complex evolution metropolis	Global	Vrugt et al., 2003
Multilevel coordinate search	Global	Lambot et al., 2002

Requirements for the appropriate use of inverse modelling

Existence of a solution of the forward model in the parameter domain

The first condition a model must meet is that the forward solution exists for the boundary conditions and initial conditions corresponding to the experiment, including throughout the range for all of the parameters. The parameter domain in this context is a subset of the space of real values containing all possible values of model parameters. As an example, for DegT50, the parameter domain could stretch from the minimum value ever observed until the maximum value ever observed, in conditions similar to what occurred during the experiment. During inverse modelling, an optimal parameter is selected from all possible values within this parameter domain.

The FOCUS leaching models use numerical solutions to solve the soil pesticide fate and transport equations. The numerical solutions may suffer from convergence problems for the specified conditions in some parts of the parameter domain (e.g. Vanderborght, 2004). If the solution of the forward model becomes unstable in part of the parameter domain then

difficulties will occur with the inverse model if the optimal parameter is found in this part of the parameter domain.

Adequacy of the forward model for describing the experiment

Obviously the forward model needs to be adequate for describing the experiment, which means that the leaching model must be reasonably validated for the conditions of the experiment. FOCUS leaching models have been subjected to a series of model validation studies in the past (e.g. Vanclooster et al., 2000; Trevisan et al., 2003) and have often proven to be well validated for experimental conditions in the validation experiments. Yet, the conditions of the inverse modelling experiment may differ significantly from the validation experiments. In such cases, inverse modelling may be inappropriate.

FOCUS leaching models view the transport of pesticide as a one-dimensional vertical transport process through a vertical heterogeneous soil profile. Hence, for inverse modelling, only leaching experiments which comply with this hypothesis can be considered. Inverse modelling is not appropriate when reasonable evidence exists that processes which are not considered in the leaching model influence the leaching event in the experiment. A typical example is the occurrence of preferential flow in a cracking clay soil. If a field or lysimeter experiment is conducted on a cracking clay soil, then this experiment will be of little use for estimating the fate and transport parameters of a chromatographic flow model. Another example is the use of a field experiment along a hill slope, where reasonable evidence exists for horizontal flow in the subsurface (e.g. interflow).

Uniqueness of the forward and the inverse model

Different parameter sets must lead to different solutions of the forward model, if not parameters are unidentifiable and the inverse modelling is inappropriate. Problems can therefore occur when more than one solution of the forward model exists. To clarify, consider the following example. Suppose total leaching has been measured during a crop season on a one-dimensional lysimeter experiment. The initial model simulation with a given DegT50 and K_d overestimates the total leaching. In this case, a better simulation could be obtained if DegT50 is decreased or K_d increased, or both. Hence, for a given DegT50, different results of total leaching can be obtained by modifying K_d. In this case, the modelling of total leaching during the crop season in terms of DegT50 is not unique and DegT50 values cannot be correctly identified from total leaching alone, unless additional information is available such as the time course of the leaching event within the crop season. In addition, a

reliable estimate of individual parameters cannot be obtained when different parameter combinations lead to the same solution.

Sensitivity of the model

Sensitivity means that the model should depend on the parameters, i.e., the derivative of the model response to the parameters should be different from zero somewhere in the parameter domain. A lack of sensitivity results usually in not being able to estimate the parameters. Since the object function is expressed in terms of the forward model, a lack of sensitivity of the forward model will result in a lack of sensitivity of the inverse model. Consider the example where the fraction of water filled macropores for a macropore model needs to be estimated from a field experiment where only soil volumetric moisture data have been measured. The activation of macropores in this case will hardly be visible when observing only volumetric soil moisture content since macropores contribute only to a very small fraction of the total water filled porosity. Hence, macroporous flow is not sensitive to volumetric soil moisture data and therefore soil moisture data alone does not allow estimation of macropore parameters by inverse modelling.

Robustness or stability of the inversion

The solution will be stable if it depends continuously on the measured system response so that it is not very sensitive to measurement and modelling errors, i.e., small measurement and modelling errors do not result in large changes of the optimised parameters.

Assessing the validity of inverse modelling results

Uncertainty analysis

Uncertainties in the optimised parameter set originate from either experimental errors (or measurement errors) or model errors (including errors in the numerical resolution, amongst others). Both may have a systematic and a random component. However, only the statistical or random error can be assessed statistically. Formulating the objective function as a maximum likelihood estimator enables the evaluation of the adequacy of a model for some given observations (Press et al., 1992; Hollenbeck and Jensen, 1998). At the global minimum, the objective function follows a Chi-square distribution, and the probability of model adequacy is then expressed as:

$$p_{adeq} = 1 - Q\big(\min \Phi(\mathbf{p}), N - P\big)$$

where $Q\big(\min \Phi(\mathbf{p}), N - P\big)$ is the Chi-square cumulative density function, N is the number of observations, and P is the number of optimized parameters. The definition of the threshold probability for an adequate model is subjective, but usually criterion $p_{adeq} > 0.5$ is used. If the measurement errors are normally distributed and if the model is linear in its parameters or the sample size is large enough such that the uncertainties in the fitted parameters do not extend outside a region in which the model could be replaced by a suitable linear model, then an approximate confidence interval can be defined analytically (Press et al., 1992).

Response surface analysis

Response surface analysis allows documentation of the problems related to non-uniqueness, model sensitivity, and parameter dependency in an objective and transparent way. Response surfaces are two-dimensional contour plots representing the objective function as a function of two parameters, while all the other parameters are held constant at their true value. Therefore they represent only cross sections of the full *M*-dimensional parameter space.

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APPENDIX 11. EXAMPLE OF PARAMETER ADJUSTMENT BY INVERSE MODELLING

This appendix provides an example of the procedure described in Section 8.3.3.4 and is taken from Kahl et al., 2009).

For a substance Y the DegT50 values from laboratory studies ranged from 18 to 60 days with an average (geomean) of 47 days. Average values for $K_{f,OC}$ and 1/n values were 23 dm³/kg and 0.92, respectively. Calculations with the laboratory parameters at Tier 1 of the FOCUS ground water assessment scheme indicated a leaching potential.

A lysimeter study was performed over 3 years according to the German lysimeter guideline (soil = sandy loam A). One lysimeter (A) received applications in year 1 and 2, whereas two replicate lysimeters (B and C) were applied in the first year only. Annual average concentrations in the leachate from individual lysimeters were below 0.1 µg/L (< 0.001 to 0.04 µg/L). K_{om} and DegT50 at reference conditions had been measured in the lysimeter topsoil were (K_{om} =18 dm³/kg; DegT50 = 55 days.

The data from one field lysimeters (column A) were used to estimate the substance parameters DegT50 [day] and the Freundlich sorption coefficient K_{om} [L/kg] by inverse modelling together with the uncertainties of the optimized parameter values. The model PEARL (Tiktak et al., 2000) was used for these calculations.

Three different algorithms for inverse parameter optimization were considered by Kahl et al. (2009) . The first algorithm (PEST) is a Levenberg-Marquardt (LM) procedure which is relatively fast, but may get caught in local optima. The second algorithm (PDMS2) starts multiple PEST runs with different starting values, which gives a higher probability of obtaining the global optimum. The third algorithm is SCEM (shuffled complex evolution metropolis), which has the highest probability of finding the global optimum, but is also the most demanding in computation time.

The Levenberg Marquardt-method (LM) uses a Jacobian approach and approximates the objective function based on a linearization of the model around the optimized parameter set. This linearization may result in unrealistic estimates of the parameter uncertainty when the range of the parameters in the uncertainty intervals is far beyond the range in which the linear approximation of the model is valid.

In an extension of the work of Mertens et al (2009), the pesticide parameters are optimised for the different soil horizons with respect to adsorption and for the soil layers with an assumed decrease of degradation with depth according to FOCUS (2000). The target substance parameters are the adsorption coefficient K_{om} and the normalized DegT50 (at reference conditions of 20 °C and pF 2) for the top soil layer.

Calibration

In a first step the water balance was adjusted by optimizing the crop factors with the data of the cumulative outflow from the lysimeter. Four crops with each four crop factors led to a large number of adjustable parameters. Optimisation of these parameters is difficult due to the relatively few observations. Best results are achieved by PDMS2, while SCEM performed worst, by extremely long run times. This is a hint that the default values given in PEARL are a very good starting point. The optimized values of the crop factors obtained by PDMS2 are used in further calculations.

In a second step the parameters hydraulic conductivity (k_s [cm/day]) and saturated water content (θ_s [-]) of each soil horizon were adjusted. For the four horizons this gives a total eight adjustable parameters. As starting values the van Genuchten parameters as calculated by HYPRES were chosen. All algorithms lead to results with both unrealistically high and low parameter values. Further PEST indicated that correlation between horizons is relatively high. Since the calculation with the initial values yielded similarly good modelling results, the initial parameter values from HYPRES were used in further calculations.

The simulated versus measured hydrology of the lysimeter used for the inverse modelling of the substance parameters DegT50 and K_{om} is shown in Figure A11-1.
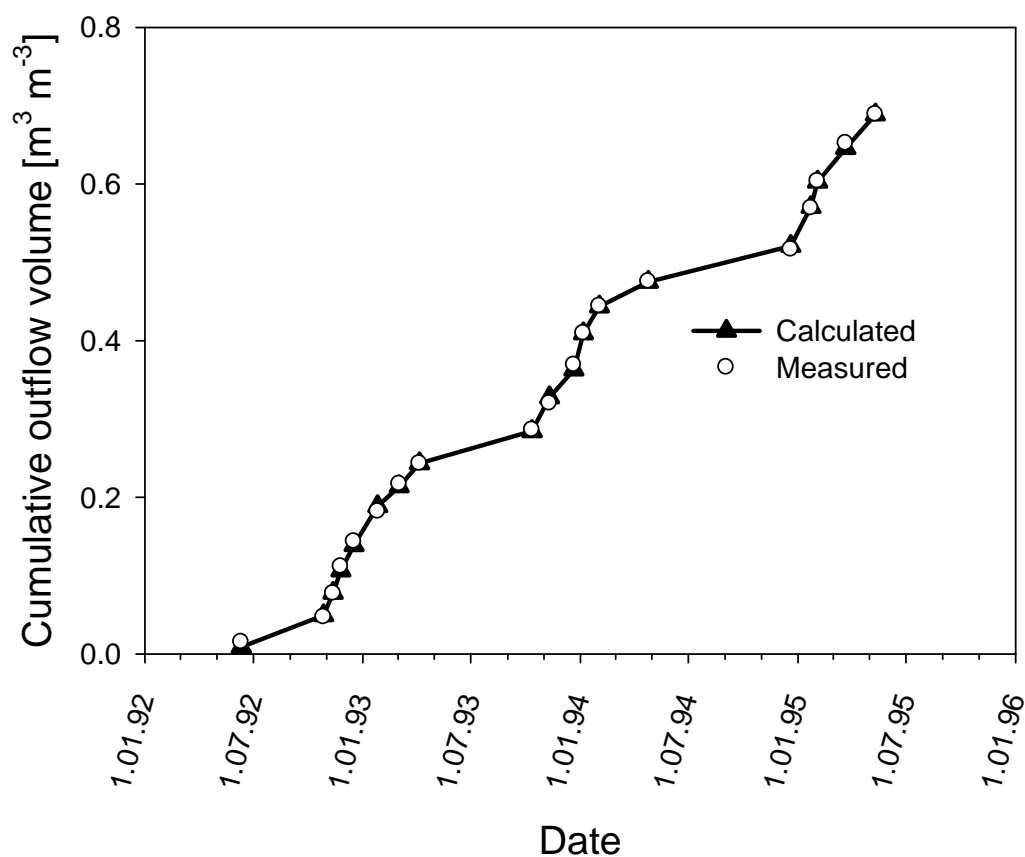
Figure A11-1. Calibration of simulating the cumulative water leaching in one of the lysimeters.

In a third (and final step) the substance parameters *DegT50* [day] and the Freundlich sorption coefficient K_{om} [L/kg] were estimated.

The simulated and the measured substance concentrations using the parameters determined in laboratory studies with the lysimeter soil (DegT50 of 55 d, K_{om} of 18 L/kg) are shown in Figure A11-2. The leaching of the compound Y in the lysimeter leachate is considerably overestimated using the DegT50/K_{om} determined with the lysimeter soil in the laboratory studies.
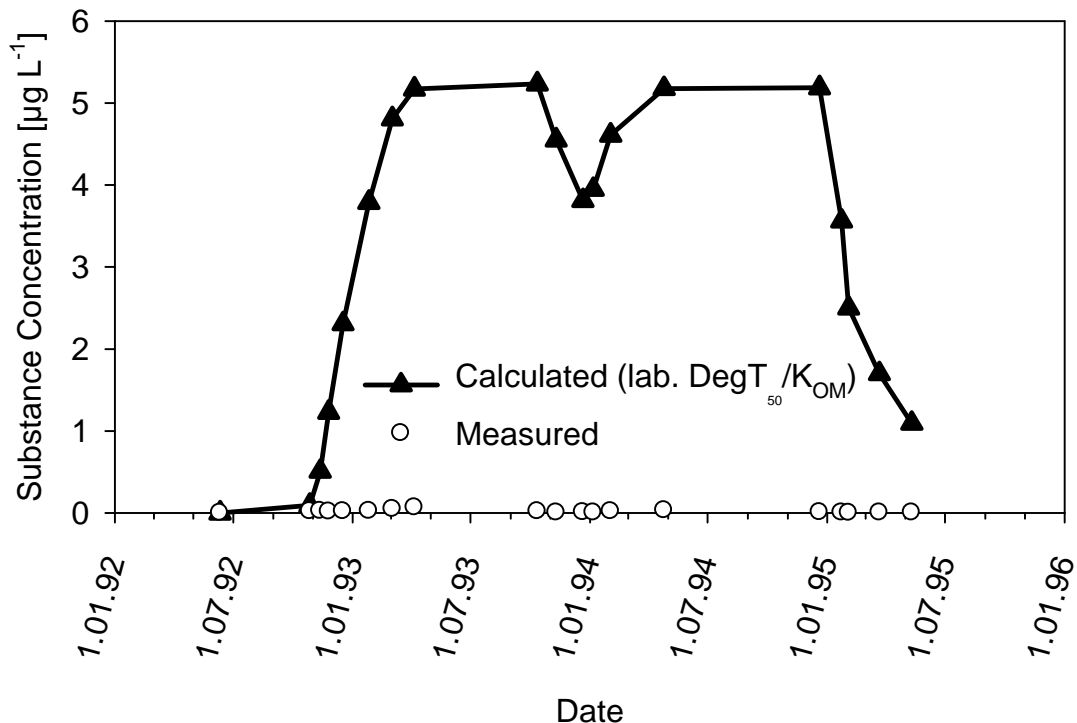
Figure A11-2. Measured and simulated concentrations of the substance in lysimeters using parameters obtained from laboratory studies with the lysimeter soil (DegT50 of 55 days, K_{om} of 18 L/kg) .

To improve the pesticide parameters by inverse modelling approach three options (PEST, PDSM2 and SCEM) were considered. A substantial improvement of the simulated breakthrough curve compared to measurements could be obtained by all optimisations.

In this example the two adjustable parameters (DegT50 and K_{om}) led to a relatively simple response surface of the objective function without many local optima (which can not be guaranteed a-priori). Hence, all three algorithms (PEST, PDSM2 and SCEM) found the same optimum. Optimum parameter values are 11.7 days for *DegT50* and 17.4 L/kg for *K_{om}*.

Measured and simulated concentrations of the substance in lysimeters using parameters obtained by inverse modelling are shown in Figure A11-3.
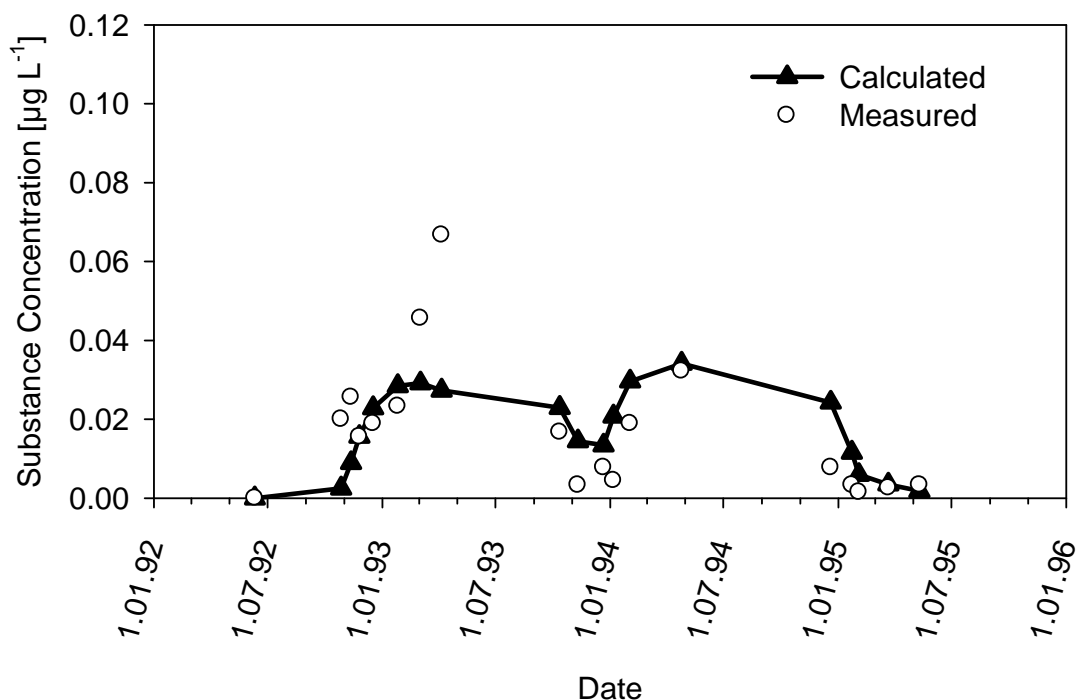
Figure A11-3. Measured and simulated concentrations of the substance in lysimeters using calibrated parameters (DegT50 of 11.7 days, K_{om} of 17.4 L/kg).

The uncertainties of the inverse estimated parameters are important information that must be provided to judge the quality of the parameter estimation approach.

From SCEM the 95% confidence intervals of the parameters can be obtained from the cumulative distribution of the sampled points (see Mertens et al., 2009) and is the preferred option (see Section 8.3.4.2). The PEST shell provides 95% confidence intervals, however as mentioned before the Levenberg-Marquardt approach in PEST may result in unrealistic estimates of the parameter uncertainty.

The cumulative distribution function (CDF) and the probability density functions (PDF) for the DegT50 and for the K_{om} and the 95% confidence intervals of the inverse estimated parameters provided by SCEM (preferred option) are shown in Figures A11-4 to A11-5 and Figures A11-6 to A11-7, respectively. The CDF and PDF of the parameters are very narrow and the 95% confidence intervals of SCEM show that the parameters were estimated with considerable certainty.

For illustrative purposes the 95% confidence intervals given by PEST are also included in the CDF graphs (Figures A11-4 and A11-5), showing a considerable wider 95% confidence interval, as a result of the problems related to the methodology.
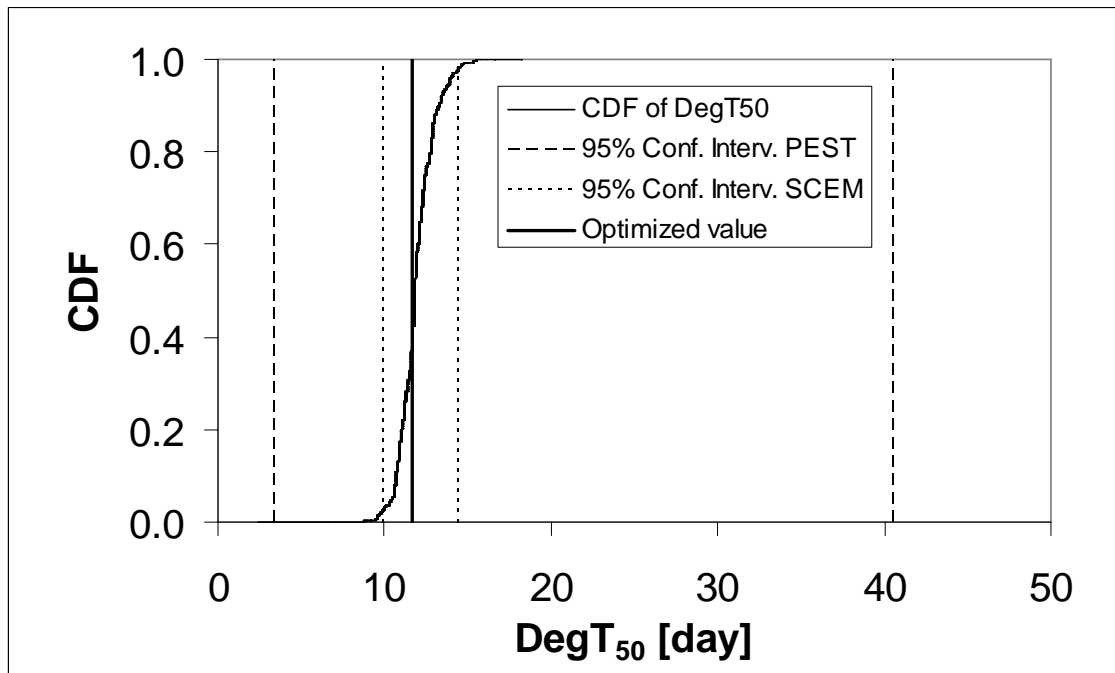
Figure A11-4. Cumulative distribution function (CDF) and 95% confidence intervals of optimised DegT50 parameter obtained by PEST and by SCEM.
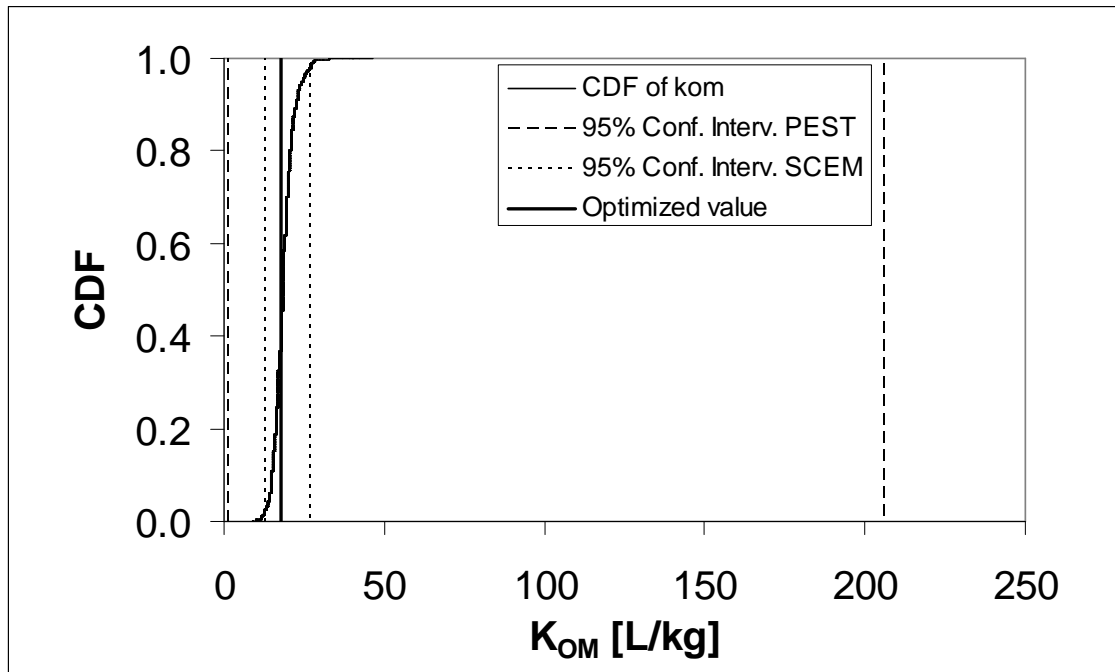
Figure A11-5. Cumulative distribution function (CDF) and 95% confidence intervals of optimised K_{om} parameter obtained by PEST and by SCEM.
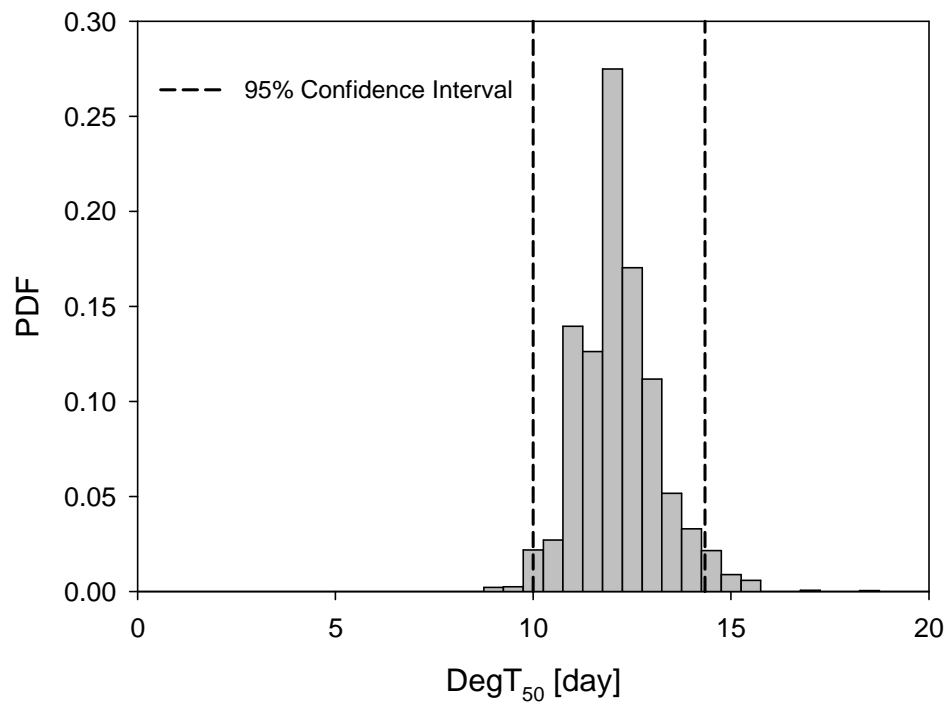
Figure A11-6. Probability density function (PDF) and 95% confidence intervals of optimised DegT50 obtained by SCEM.
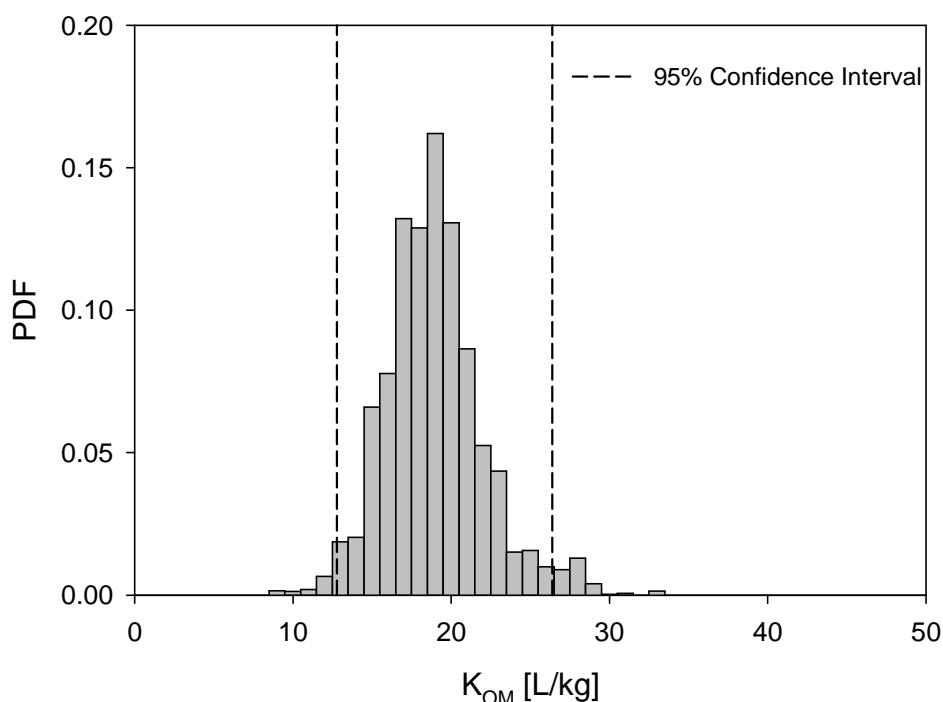
Figure A11-7. Probability density function (PDF) and 95% confidence intervals of optimised K_{om} obtained by SCEM.

Validation – context setting with independent data

Batch equilibrium data.

Batch sorption studies were performed to get further insight into the leaching and degradation behaviour of substance Y. The $K_{F,OM}$ values range from 10 - 63 L/kg with average values for $K_{f,OM}$ and 1/n values of 22 dm³/kg and 0.92, respectively.

Data from field dissipation studies.

Dissipation of compound Y was investigated also in <u>field studies</u> under a range of environmental conditions (four studies in Europe, average air temperatures 14.0-19.1°C; three studies in the US, 11.5-16.6°C; three studies in Canada, 3.4-7.7°C). In Europe, sampling started in spring after a single application and continued until residues fell below the limit of quantification (usually <100 days). Multiple applications were made in the US and Canada. Samples were taken up to >360 d after the last treatment in September. Field

458

dissipation rates were corrected to degradation rates at the reference temperature at 20°C based on a Q10 value of 2.58 and moisture of pF2.

Daily degradation rates were calculated with the ModelMaker® program using measured daily temperatures and soil moisture estimated with the PEARL model. The degradation rate at the reference temperature and moisture was optimised to fit to the experimental data. First-order DegT50 values obtained with and without temperature/moisture normalization are listed in Table A11-1.

Table A11-1. Field SFO DegT50 values of substance Y reported and normalized to reference temperature of 20°C and moisture of pF 2.

Site	Application time/ sampling period	Average temperature [°C]	DisT50 [days]	DegT50normalised [days]
EU1	spring / < 100d	17.7	14.2	10.8
EU2	spring / < 100d	19.1	7.3	4.7
EU3	spring / < 200d	14.0	37.5	25.5
EU4	spring / < 100d	16.6	4.9	3.6
US5	autumn / > 360d	13.5	19.6	11.5
US6	autumn / > 360d	11.5	12.8	8.3
US7	autumn / > 360d	16.6	7.1	9.2
CAN8	autumn / > 360d	7.7	25.6	12.4
CAN9	autumn / > 360d	8.8	15.4	6.8
CAN10	autumn / > 360d	3.4	54.4	8.1
geometric mean				**8.8**

K_{fom} and DegT50 values derived using the different approaches are summarised in Table A11-2. Sorption and degradation values for substance Y (K_{fom} and DegT50) derived by the inverse modelling approach are in agreement with the measured data from the batch equilibrium sorption studies and the normalised field degradation studies. They can be used for the calculation of PEC in ground water as outlined in Section 8.3.4.

Table A11-2. K_{fom} and DegT50 values derived using different approaches

Study type	Parameter	All value average (range)	Lysimeter soil
Batch equilibrium sorption	K_{fom} [L/kg]	22 (10-63)	18
	1/n	0.92 (0.76 - 0.97)	0.91
Laboratory degradation	$DegT50_{normalised}$ [d]	47 (18-60)	55
Field degradation	$DegT50_{normalised}$ [d]	8.8 (4.7 - 25.5)	-
Inverse Modelling Monolith Lysimeter	$DegT50_{normalised}$ [d]	-	11.7
	K_{om} [L/kg]	-	17.4

References

Mertens, J.; Kahl, G.; Gottesbüren, B.; Vanderborght, J. 2009. Inverse modeling of pesticide leaching in lysimeters: local versus global and sequential single-objective versus multi-objective approaches.- Vadose zone journal (accepted).

Kahl, G.; Sidorenko, Y.; Jene, B.; Gottesbüren, B. 2009. Inverse modeling of pesticide leaching in lysimeters with different optimization algorithms. (in preparation).

APPENDIX 12. THEORETICAL BASIS FOR A VULNERABILITY CONCEPT

J. Vanderborght

The purpose of the FOCUS ground water scenarios is to identify whether conditions, which are relevant for the intended use of the product, exist that guarantee a safe use. A 'safe use' guarantees that the overall protection goal, i.e. the concentration of a pesticide in the ground water should not exceed 0.1 µg/L is met. The main problem is to define what is meant by 'relevant for the intended use' and the criteria for determining 'safe'.

Since guaranteeing that under all conditions the protection goal is reached is impossible, the FOCUS ground water scenarios use a 90 % vulnerability concept (as opposed to a 100 % vulnerability concept which guarantees that the protection goal is met for all possible conditions). Different scenarios approximating this 90 % vulnerability concept have been developed to produce 'reasonable worst case' scenarios representing 'major agricultural regions' in Europe with different climatic and pedologic conditions. When applications to a specific crop for one of these scenarios were shown not to exceed 0.1µg/L, this use was considered to be 'safe' and 'relevant for the intended use' of the product in the European Union. However, since these 'major agricultural regions' have not been geographically delineated, they are rather virtual and the relevance of the scenarios cannot be checked. What is actually meant by '90 % vulnerability' and 'areas relevant for intended use' is not defined in a clear cut manner and the lack of this definition is the basis for numerous discussions.

The purpose of this appendix is to try and define 90 % vulnerability for areas which are relevant for the intended use and which are geographically delineated if the pesticide leaching towards the ground water were known at every location in this area. This vulnerability concept for a hypothetical perfect knowledge of pesticide leaching may form the basis for a concept that is based on incomplete and uncertain knowledge. This appendix is not intended to delineate and geographically define 'areas relevant of intended use' that are represented by a certain scenario.

Since pesticide concentrations in the water that recharges the ground water vary both in space and time, both the temporal and spatial variability are considered in the vulnerability concept. Based on two extreme mixing concepts, two extreme vulnerability concepts can be considered: the 100 % and 50 % vulnerability. The first concept (termed here 100 %

vulnerability) neglects all mixing process that may dilute concentrations with time and in space in the ground water. According to this concept, the concentration must be smaller than 0.1 μg/L at every time, t, and at each location, $\mathbf{x_a}$ where the substance is applied to satisfy the ground water protection limit:

$$C(\mathbf{x_a};t) < 0.1 \text{ μg/L for all } \mathbf{x_a} \text{ and t.} \qquad \text{(A12-1)}$$

The second concept (termed here 50 % vulnerability) assumes that all water recharging the ground water is instantaneously mixed with the entire ground water reservoir or body of the region. In this concept, the protection limit is achieved when the flux weighted temporally and spatially averaged concentration is smaller than 0.1 μg/L:

$$\frac{\iint\limits_{\mathbf{A_a}\,t} J_w(\mathbf{x_a};t)C(\mathbf{x_a};t)dtd\mathbf{x_a}}{\int\limits_{\mathbf{A_{tot}}}\int\limits_t J_w(\mathbf{x};t)dtd\mathbf{x}} < 0.1\mu gL^{-1} \qquad \text{(A12-2)}$$

where J_w is the vertical water flux or the recharge rate, $\mathbf{A_a}$ is the region where the substance is applied and $\mathbf{A_{tot}}$ the entire region. In the 100% vulnerability concept, no ground water is exceeding the ground water limit at any time whereas in the 50% concept, the overall concentration in the entire ground water body is on average below the ground water limit. Although these concepts can be exactly defined and unequivocally interpreted, they are irrelevant in practice. High concentrations exceeding the ground water limit can occur sporadically in the percolating water. But, the amount of water carrying these high concentrations may only be a minimal fraction of the directly receiving ground water body and of the total amount of water percolating through the soil over a longer time period so that the high concentrations may be effectively diluted. On the other hand, the lateral extent of ground water bodies is much larger than their vertical extent so that the mixing of ground water in the lateral direction may be considerably limited. This implies that recharge in subregions where the pesticide is not applied may not or only very limited dilute the recharge under fields where the substance is actually applied, or the ground water in 'vulnerable' areas where the ground water limit is exceeded cannot mix with ground water in less 'vulnerable' areas where the limit is not exceeded.

The definition of an applicable vulnerability concept comes down to identifying the size of an elementary area, ΔA_a, and elementary time interval, Δt, over which the pesticide and water fluxes are averaged and to identifying the proportion of the time intervals and averaging

areas to the overall considered time period and application area in which exceeding the ground water limit is tolerated:

$$\frac{\int_{\Delta A_a}\int_{\Delta t}J_w(\mathbf{x_a};t)C(\mathbf{x_a};t)dtd\mathbf{x_a}}{\int_{\Delta A_a}\int_{\Delta t}J_w(\mathbf{x};t)dtd\mathbf{x}} < 0.1\mu g L^{-1} \text{ for x\% of all } \Delta A \text{ and } \Delta t \qquad \text{(A12-3)}$$

These spatio-temporal averaging intervals should be based on the size or volume of an elementary completely mixed ground water volume, ΔV that needs to be protected:

$$\Delta V = \int_{\Delta A_a}\int_{\Delta t}J_w(\mathbf{x_a};t)dtd\mathbf{x_a} \qquad \text{(A12-4)}$$

A problem with the vulnerability concept in Equation A12-3 is to divide the probability over the spatial and temporal elementary intervals. By defining an elementary completely mixed ground water volume as the protection goal, the temporal and spatial variability of the pesticide leaching can be effectively integrated in the vulnerability concept since a ground water volume represents the integrated vertical water flux or ground water recharge over time that is in turn integrated over a certain area.

$$\frac{\int_{\Delta A_a}\int_{\Delta t}J_w(\mathbf{x_a};t)C(\mathbf{x_a};t)dtd\mathbf{x_a}}{\int_{\Delta A_a}\int_{\Delta t}J_w(\mathbf{x};t)dtd\mathbf{x}} < 0.1\mu g L^{-1} \text{ for x\% of all } \Delta V \qquad \text{(A12-5)}$$

In the 100 % vulnerability concept, an infinitesimal ground water body is protected whereas in the 50 % concept, the totally mixed entire ground water body is protected. The elementary mixed ground water body can be directly interpreted in practical terms. For instance, for a drinking water production well, it may be interpreted as the ground water volume in the capture zone of the well. The capture zone of the well corresponds with the elementary area over which the ground water recharge and pesticide fluxes are averaged and the time interval corresponds with the time that is needed to refresh the entire ground water body by ground water recharge in the well capture zone. A 90 % vulnerability concept could be defined so that at any time, 90 % of the potential wells in the area where the substance is applied would produce water with pesticide concentrations below the drinking water limit. If the time needed to refresh the ground water volume is much larger than the time scale in

which most variability of the recharge occurs, e.g. more than 10 years, then the temporal variability of temporally averaged pesticide fluxes over the elementary time interval at a certain location can be neglected compared with the spatial variability of the temporally averaged pesticide fluxes. In that case, only the spatial component plays a role in the vulnerability concept whereas the temporal fluctuations are averaged out. Since the yearly ground water recharge is mostly only a small fraction of the total ground water body, the assumption that temporal fluctuations of yearly flux weighted averaged pesticide concentrations are important or should be considered in the vulnerability assessment is not reasonable in view of a vulnerability concept that is based on a practical definition of an elementary mixed ground water volume. In that perspective, the 80 % spatial percentile of the 80 % percentile of the yearly averaged concentrations at a certain location, which is considered as an 'overall 90 % percentile', can hardly be linked to a concrete protection goal. In view of the previous discussion, using the 90 % spatial percentile of the long term averaged flux weighted averaged concentrations may be a more relevant approach for a '90 % vulnerability concept'. Note that not only spatial variability of soil properties but also the spatial variability of climatic conditions needs to be considered.

APPENDIX 13. REVIEW OF PROCEDURE FOR SELECTING THE 80TH PERCENTILE CONCENTRATION FROM A TIME SERIES OF CONCENTRATIONS

The FOCUS ground water scenarios aim at using the 80th percentile leaching concentration from a series of 20 concentrations. There are a number of methods used to calculate assign percentiles to a series of data. The work group considered three methods: Hazen, Weibull, and Harrell-Davis.

For the first two methods a data point j in a ranked series of n data points represents a probability of:

Hazen: 100 (2j - 1) / 2n

Weibull: 100 j / (n + 1)

Table A13-1. Calculation of percentiles from a series of 20 data points.

Rank Number	Cumulative Probability Estimate (percent)	
	Hazen	Weibull
1	2.5	4.76
2	7.5	9.52
3	12.5	14.29
4	17.5	19.05
5	22.5	23.81
6	27.5	28.57
7	32.5	33.33
8	37.5	38.10
9	42.5	42.86
10	47.5	47.62
11	52.5	52.38
12	57.5	57.14
13	62.5	61.90
14	67.5	66.67
15	72.5	71.43
16	77.5	76.19
17	82.5	80.95
18	87.5	85.71
19	92.5	90.48
20	97.5	95.24

Thus the Hazen procedure suggests that an average of the ranked numbers 16 and 17 is a good estimate of the 80th percentile, while the Weibull approach suggests the 80th percentile is 0.2 x 16th number + 0.8 x 17th number. The previous FOCUS Groundwater Scenarios Workgroup (FOCUS, 2000) was aware that the 17th value was a conservative estimate of the

80th percentile value but decided to use number 17 for simplicity. However, for percentile calculations in higher tiers or in GIS-based approaches there is no need to stick to this more simple and conservative procedure.

The third method, by Harrell and Davis (1982), is significantly more complicated. To check the implications of this approach, the cumulative probability was calculated for the percentiles in Table A13-1 with for an example distribution of 20 values (1-20). Results are presented in Table A13-2.

Table A13-2. Calculated percentile values for the distribution 1-20 using Harrell-Davis.

Percentile	Cumulative Probability Estimate
2.5	1.215942
7.5	2.016945
12.5	2.998509
17.5	3.999759
22.5	5.000018
27.5	6.000003
32.5	7.000000
37.5	8.000000
42.5	9.000000
47.5	10.000000
52.5	10.999999
57.5	11.999999
62.5	13.000000
67.5	14.000000
72.5	14.999996
77.5	15.999981
82.5	17.000246
87.5	18.001493
92.5	18.983049
97.5	19.784061

The choice of which method is most scientifically suitable is beyond the expertise of the work group. Weibull is widely used by engineers and is recommended over Hazen for use by hydrologists by Han (1977). Harrell and Davis (1982) state that their approach is superior to the approach of Weibull. Recently this approach was adopted by the EU for estimating percentiles for residues in food. For the distribution tested, Table A13-2 shows that Harrell-Davis gave the same answer as would be obtained by Hazen between the 12.5 and 87.5 percentiles. Therefore, the work group decided that the 80th percentile concentration would be considered as the average of the 16th and 17th ranked concentration values.

References

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2, 202pp.

Han, C. T. 1977. Statistical Methods in Hydrology. Iowa State University Press, Ames IA,

Harrell, F. E., Davis, C. E. 1982. A New Distribution-Free Quantile Estimator. Biometrika 69:635-640.

APPENDIX 14. AVERAGING OF SIMULATIONS WITHOUT ANNUAL APPLICATIONS

The vulnerability concept leaves open the option of how to deal with averaging in those cases where a product is applied every second or third year. The work group considered two approaches. One was the approach recommended by FOCUS (2000) in which flux-weighted averages were calculated for each of the 20 two or three year periods, then ranked, and the 80th percentile value chosen. The other was taking the 80th percentile of the 40 or 60 yearly values. Potentially the approaches could have quite different results. For example, if essentially all of the movement to ground water occurred in one year of the two or three year period, the first approach would end up being the concentration for 80th percentile year divided by two or three while the second approach would be the 40th or 27th percentile year of the 20 years with residues (but not divided by two or three as in the first case). To determine the differences between the two approaches, a test case was evaluated using FOCUS PRZM consisting of compound D from FOCUS (2000) applied to summer potatoes every third year at an application rate of 1 kg ai/ha. The ratio of annual concentrations approach to the three-year average approach ranged from 0.02 to 1.12 (Table A16-1). In general both approaches gave about the same answer with a couple of cases being substantially lower using annual concentrations. Since there was not much difference between the methods and the reasons to choose one approach over another are not particularly compelling, the work group decided not to change the averaging of simulations from the approach of ranking 20 multi-year values as recommended by FOCUS (2000). Note that this exercise was performed with the determination of the 80th percentile as recommended by FOCUS (2000). The change in the calculation of 80th percentile proposed in this report should have minimal effect on the conclusion from this example.

Table A14-1. Results obtained with the two averaging methods for Compound D applied every third year to summer potatoes at a rate of 1 kg ai/ha.

Location	80th Percentile Concentration (ppb)		Ratio***
	Method 1*	**Method 2****	
Châteaudun	2.1 E-04	2.1 E-04	0.97
Hamburg	2.0 E-03	2.4 E-03	0.85
Jokioinen	9.2 E-06	9.7E-06	0.95
Kremsmünster	1.1 E-04	1.8 E-04	0.58
Okehampton	2.5 E-03	2.2 E-03	1.12
Piacenza	8.3 E-03	2.6 E-02	0.31
Porto	4.8 E-10	6.7 E-10	0.71
Sevilla	1.4 E-11	7.0 E-10	0.02
Thiva	8.1 E-09	1.1 E-08	0.77

*Annual average approach: 12th highest of 60 concentrations.

**Multi-year average approach: 4th highest of 20 three-year flux-weighted concentrations.

***Concentration from method 1 divided by concentration from method 2.

References

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2, 202pp.

APPENDIX 15. REVIEW OF THE PORTO AND PIACENZA FOCUS GROUND WATER SCENARIOS

The remit of the FOCUS Ground Water Work Group included reviewing the relative vulnerability of the Piacenza and Porto scenarios considering the work of the APECOP project (Vanclooster et al., 2003). If needed new scenarios should be developed, but changes should be kept to a minimum. This section describes a quantitative re-analysis of the soil leaching vulnerabilities for the Piacenza and Porto scenarios and makes recommendations for modifying the scenarios in order to achieve the target 80th percentile soil vulnerability.

Background

The FOCUS Groundwater Scenarios Workgroup defined Tier 1 ground water modelling scenarios at nine locations. These scenarios were designed to describe an overall vulnerability approximating the 90th percentile of all possible situations, in order to collectively represent realistic worst-case combinations of soil and climatic conditions for leaching in the EU (FOCUS, 2000). Since the Tier 1 standard scenarios are intended to be used for a wide range of compounds and crops, a generalised and pragmatic approach to scenario selection was required, in contrast to the higher-tier crop- and compound-specific methodologies discussed elsewhere in this document. The scenarios do not mimic specific fields, and nor are they necessarily representative of the agriculture at the location after which they are named or in the member states where they are located.

The exact percentile for the soil properties and weather which provide an overall vulnerability of the 90th percentile cannot be determined precisely without extensive simulations of the various combinations present in a specific region, and will anyway vary depending on the compound properties and crop that are simulated. After exploratory statistical analysis, the work group decided that the overall 90th percentile at the generic Tier 1 level could be best approximated by using an 80th percentile vulnerability for weather and an 80th percentile vulnerability for soil. The 80th percentile vulnerability for weather was determined by performing simulations using multi-year weather data and selecting the 17th highest annual concentration from 20 years of results, while the 80th percentile vulnerability for soil was selected by expert judgement.

The FOCUS Groundwater Scenarios Workgroup acknowledged that reviewing the selection procedure at a future date in light of new findings and better data availability may be

appropriate. Subsequently, the APECOP project conducted research aimed at validating the selection of realistic worst case ground water modelling scenarios, by comparing PEC$_{GW}$ for each FOCUS scenario against the 90th percentile value found within the respective agro-climatic zone using a spatial modelling approach (Table A15-1). The results of the APECOP project indicate that the Piacenza scenarios generally represent an extreme, *i.e.* unrealistic worst-case within the respective agro-climatic zone. By contrast, the results indicate that the Porto scenarios generally do not represent a sufficiently worst-case situation within the respective agro-climatic zone in relation to the target 90th percentile.

Table A15-1. Extent of the FOCUS agro-climatic zones. Source: Table 2.1 from FOCUS (2000).

Precipitation (mm)	Mean Annual Temperature (°C)	Arable land * (%)	Total Area * (%)	Representative Locations
601 to 800	5 to 12.5	31	19	Hamburg/Châteaudun
801 to 1000	5 to 12.5	18	13	Kremsmünster
1001 to 1400	5 to 12.5	15	12	Okehampton
601 to 800	> 12.5	13	11	Sevilla/Thiva **
801 to 1000	> 12.5	9	8	Piacenza
< 600	> 12.5	4	4	Sevilla/Thiva
< 600	5 to 12.5	3	2	Châteaudun ***
1001 to 1400	> 12.5	3	3	Porto
< 600	< 5	1	11	Jokioinen
Other combinations		3	17	-

* Relative to the area of the EU-15 plus Norway and Switzerland.

** Although these locations have less than 600 mm of precipitation, irrigation typically used at these two locations brings the total amount of water to greater than 600 mm.

*** Most areas in this climatic zone will be irrigated, raising the total amount of water to greater than 600 mm. Therefore, Châteaudun can be considered representative of agriculture in this climatic zone.

Methodology

The selection of representative (80th percentile) soil properties in the original definitions of the FOCUS ground water Tier 1 scenarios was based on expert judgement due to the lack of comprehensive soil data bases at that time. A quantitative re-analysis of the soil leaching vulnerabilities of the Piacenza and Porto scenarios was performed in order to identify suitable modifications to the scenarios to achieve the target vulnerability. Since soil organic carbon

content has been found to be the most sensitive soil property in determining the leaching of pesticides (*e.g.* Piñeros-Garcet et al., 2003, as cited by Vanclooster et al., 2003; Schlosser & McCray, 2002), and lends itself to quantitative analysis using state-of-the-art European soil data bases, in this analysis topsoil organic carbon content was assumed to provide a good indicator of soil vulnerability to pesticide leaching.

The original FOCUS analysis of climatic zones was based on 5 km raster data from the EU project by Knoche et al. (1998), as described in FOCUS (2000, Section 2.1.3). These data were obtained from the Fraunhofer Institute in order to extend the analysis to the quantitative assessment of soil vulnerability for the Piacenza and Porto climatic zones, using pan-European 'OCTOP' topsoil organic carbon content data that have recently been made available (Jones et al., 2004; 2005). The data layers used in the analysis were as follows:

- Climatic zones from the Fraunhofer data (reconstructed from the long-term average temperature and precipitation data according to the values given in Table A15-1
- Arable areas from the Fraunhofer data (reconstructed from the original 0 – 255 land use classification and the aggregated land use codes provided by M. Klein)
- OCTOP data from the European Commission Joint Research Centre

Since the OCTOP data base is at 1 km resolution whereas the climatic and land use data were only available at 5 km resolution, the OCTOP data were first aggregated to 5 km resolution using average values in each cell. Values from the original data layer in the range 0 – 0.1% OC were excluded from the analysis, *i.e.* reclassified as 'no data'.

The cells with arable land use for the Piacenza and Porto climatic zones were extracted from the 5 km OCTOP layer using GIS analysis. The values were ranked and the cumulative percentages were plotted in order to determine the 20th percentile topsoil organic carbon content for each of these climatic zones, taken as equivalent to the 80th percentile soil vulnerability.

Results of the analysis

The 20th percentile OC content in the Piacenza and Porto climatic zones was calculated to be 1.26% and 1.42%, respectively. The distributions of organic carbon within the FOCUS Piacenza and Porto climatic zones are shown in Figure A15-1.

The current topsoil organic carbon content of 1% in the Piacenza soil profile is too low in comparison to the target value of 1.26%, leading to a leaching vulnerability that is too high.

By contrast, the current topsoil organic carbon content of 3.8% in the Porto soil profile is too high in comparison to the target value of 1.42%, leading to a leaching vulnerability that is too low. These findings are in line with those of APECOP (Vanclooster et al., 2003).

Piacenza climate zone
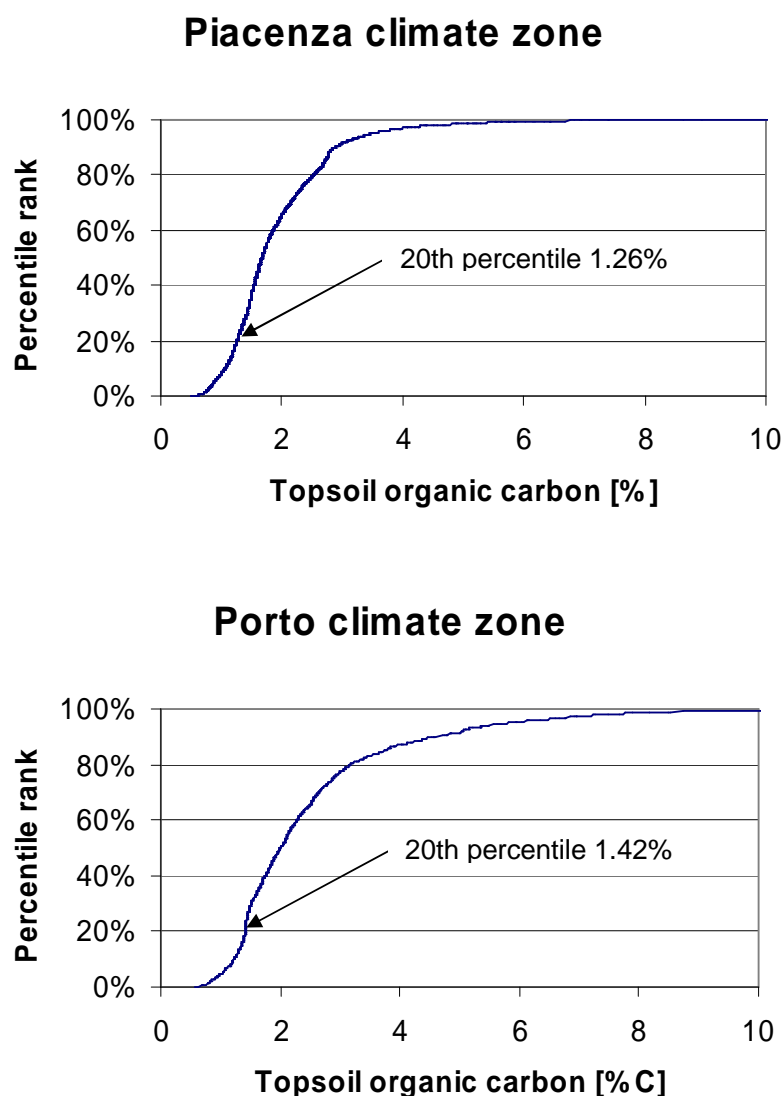
Porto climate zone

Figure A15-1. Topsoil organic carbon distributions in the FOCUS Piacenza and Porto climatic zones.

Scenario Modifications

Based on the findings of the analysis, the work group decided to modify the topsoil organic carbon contents in the existing FOCUS scenarios in line with the 20th percentile values of

1.26% for the Piacenza scenarios and 1.42% for the Porto scenarios. The subsoil organic carbon contents were changed in the same ratio as the topsoil organic carbon contents.

Since the change in soil organic matter is relatively minor in the Piacenza scenarios, other soil properties were not changed. The change in organic carbon content in the Porto scenarios is larger, therefore the soil bulk density was increased to reflect the decrease in organic carbon content, with other soil properties unaffected. The proposed modifications to the scenario soil profiles are shown in Tables A15-2 and A15-3.

Table A15-2. Proposed modifications to the Piacenza soil profile.

Horizon	Depth [cm]	FOCUS (2000)		Proposed Values	
		OC [%]	OM [%]	OC [%]	OM [%]
Ap	0-30	1.00	1.72	1.26	2.17
Ap	30-40	1.00	1.72	1.26	2.17
Bw	40-60	0.37	0.64	0.47	0.80
Bw	60-80	0.37	0.64	0.47	0.80
2C	80-100	0.00	0.00	0.00	0.00
2C	100-170	0.00	0.00	0.00	0.00

Table A15-3. Proposed modifications to the Porto soil profile.

Depth [cm]	FOCUS (2000)			Proposed Values		
	OC [%]	OM [%]	BD [g cm^{-3}]	OC [%]	OM [%]	BD [g cm^{-3}]
0 – 35	3.8	6.6	0.89	1.42	2.45	1.09
35 – 60	2.1	3.7	1.25	0.78	1.35	1.45
60 – 100	2.1	3.7	1.25	0.78	1.35	1.45
100 – 120	2.1	3.7	1.25	0.78	1.35	1.45

The soil hydraulic properties were estimated using HYPRES with the same procedures used In FOCUS (2000) (Boesten, 2006, personal communication). These results along with a comparison with the previous values are provided in Tables A15-4 and A15-5.

Table A15-4. Soil hydraulic properties (Van Genuchten/Mualem parameters) for the original and revised Piacenza soil profile.

Depth (cm)	θs ($m^3\ m^{-3}$)	θr ($m^3\ m^{-3}$)	α (m^{-1})	n	m	Water content 10kPa ($m^3\ m^{-3}$)	1600kPa ($m^3\ m^{-3}$)	Ksat ($m\ s^{-1}*10^{-6}$)	λ
0-40 Old	0.4632	0.0100	3.050	1.2487	0.1992	0.339	0.107	4.666	-1.906
0-40 New	0.4622	0.0100	3.13	1.238	0.1923	0.341	0.113	4.269	-2.037
40-80 Old	0.4546	0.0100	2.270	1.3605	0.2650	0.317	0.063	6.217	0.316
40-80 New	0.4543	0.0100	2.31	1.3531	0.261	0.317	0.065	6.138	0.109

Table A15-5. Soil hydraulic properties (Van Genuchten/Mualem parameters) for the Porto soil profile.

Depth (cm)	θs ($m^3\ m^{-3}$)	θr ($m^3\ m^{-3}$)	α (m^{-1})	n	m	Water content 10kPa ($m^3\ m^{-3}$)	1600kPa ($m^3\ m^{-3}$)	Ksat ($m\ s^{-1}*10^{-6}$)	λ
0-35 Old	0.5780	0.0100	4.830	1.1588	0.1370	0.443	0.208	2.885	-1.630
0-35 New	0.5230	0.0100	2.30	1.2888	0.2241	0.388	0.103	6.504	-1.1949
35-120 Old	0.4720	0.0100	4.340	1.2123	0.1751	0.339	0.125	3.142	-1.350
35-120 new	0.4183	0.0100	4.29	1.3078	0.2354	0.262	0.065	4.774	-0.9972

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APPENDIX 16. LITERATURE REVIEW OF DISPERSIVITY VALUES

J. Vanderborght

Introduction and Background

In all of the FOCUS ground water scenarios, except for the Châteaudun scenarios when parameterized for use with MACRO, the convection dispersion equation is used to describe the leaching of pesticides:

$$\theta \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = -\theta v \frac{\partial C}{\partial z} + \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \mu\left(\theta C + \rho_b S\right) \qquad \text{(A16-1)}$$

where θ is the volumetric water content, C the concentration in the soil water, ρ_b the soil bulk density, S the concentration of the sorbed phase, v the pore water velocity, D the hydrodynamic dispersion coefficient, and μ a first order decay constant.

The hydrodynamic dispersion coefficient D is defined as:

$$D = \lambda v + \tau(\theta)D_0 \qquad \text{(A16-2)}$$

where λ (L) is the dispersivity, v (L T^{-1}) is the transport velocity, τ a tortuosity coefficient which depends on the volumetric soil water content, θ, and D_0 (L² T^{-1}) the molecular diffusion coefficient.

A study by Boesten (2004) showed that a different parameterization of the dispersivity explained to a large extent the differences between pesticide leaching calculated by the PRZM and PELMO models (using a λ of 2.5 cm) and by the PEARL model (using a λ of 5 cm). A harmonization of the dispersivity parameterization in the different models is therefore expected to harmonize the calculated pesticide concentrations by the different models.

A data set of dispersivity values was compiled by reviewing leaching experiments that were reported in the literature. In leaching experiments, depth profiles or time series of an inert tracer are measured. From these profiles or time series, the hydrodynamic dispersion coefficient, D, and the pore water velocity v are derived. This is generally done assuming that the transport velocity v and dispersion coefficient D are constant in the soil profile and do not change with depth, i.e. a hydrodynamically homogeneous soil profile. For an effective molecular diffusion coefficient ($\tau(\theta) D_0$) of 0.5 cm² d^{-1}, the contribution of the diffusion to the hydrodynamic dispersion D observed in the leaching experiments was on average 5%. Therefore, the dispersivity, λ, was simply derived from the ratio D/v assuming that the molecular diffusion can be neglected.

Contents of dispersivity data base

The data base contains 635 entries derived from 57 publications in scientific journals. Since soil structure has an important impact on solute transport, only experiments in undisturbed soils were considered and experiments in repacked or refilled soil cores or columns were excluded. Besides dispersivities, also experimental factors were included in the data base so that relations between experimental factors and dispersivities can be inferred. The experimental factors form the basis for selection or exclusion of certain leaching studies which are considered to be in agreement or disagreement with the climatic and pedologic conditions that are represented by the FOCUS scenarios.

The following variables were included:
- transport distance z (cm),i.e. the vertical distance that the applied tracer travelled
- the dispersivity λ (cm)
- the transport velocity v (cm d^{-1}) derived from the tracer breakthrough or concentration depth profiles
- the pore water velocity v_p (cm d^{-1}) derived from the flow rate divided by the volumetric water content
- the ratio of v/v_p which is a measure for preferential solute transport ($v/v_p > 1$) or solute retardation ($v/v_p < 1$)
- the average flow rate J_w (cm d^{-1}) which is the net infiltrated water depth during the leaching experiment divided by the duration of the experiment
- the effective flow rate J_{weff} (cm d^{-1}) which is a measure for the flow rate intensity in the soil during the experiment (for a definition see Vanderborght et al., 2000)
- the experiment number (The same experiment number was given to dispersivities that were derived from a leaching experiment that was carried in the same soil column or field plot, at the same flow rate, and that was monitored using the same measurement technique)
- the name of the field site where experiments were carried out or from where soil samples were taken
- USDA soil texture class
- scale of the leaching experiments [Three classes were considered: core-scale (soil cores with a length < 30 cm), column scale (undisturbed soil monoliths with a length > 30 cm), and field scale]
- type of concentration that was measured: volume averaged or resident versus flux averaged concentrations

- measurement type: direct (in the effluent from soil columns or cores), coring (analysis of soil samples), samplers (extraction of soil solution in the soil profile using suction samplers or suction plates), TDR (concentrations derived from bulk soil electrical conductivity measured with TDR), tile drains, dye tracers (image analysis of photographic recordings of dye stained patterns on excavated soil surfaces), calculated (average concentrations calculated from the average of local concentration measurements)
- flow type: steady (steady unsaturated flow), ponding (steady flow under saturated flow conditions), intermittent (periodic flow under unsaturated conditions), interpond (periodic ponding of the soil surface), climatic (natural rainfall and soil evaporation), interclim (natural rainfall and soil evaporation with intermittent additional water application)
- Author
- Year of publication

A complete list is appended to the end of this appendix.

Effect of experimental factors on dispersivity

Scale of the study, flow boundary condition type, and soil texture are considered to be the most important experimental factors. Figures A16-1 to A16-3 show the number of data entries as a function of these factors. These figures also provide the mean dispersivity observed and the mean values of the flow rate and transport distance in the experiments.
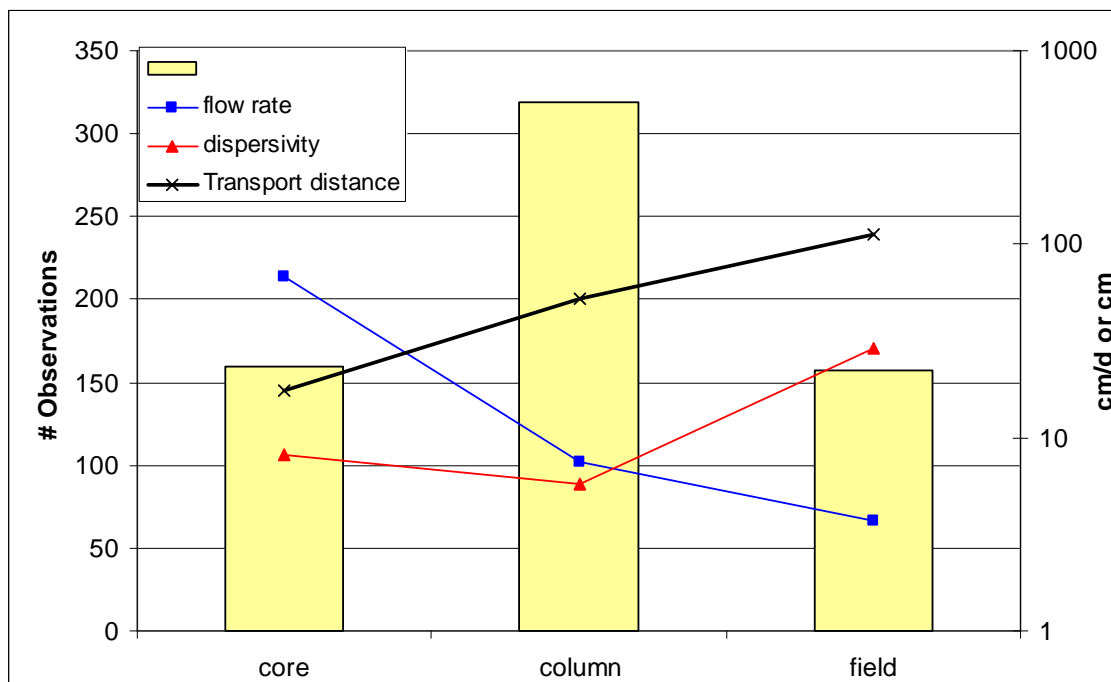
Figure A16-1. Number of observations (bars), mean flow rate (blue line), mean transport distance (black line), and mean dispersivity (red line) in the experiment scale classes.
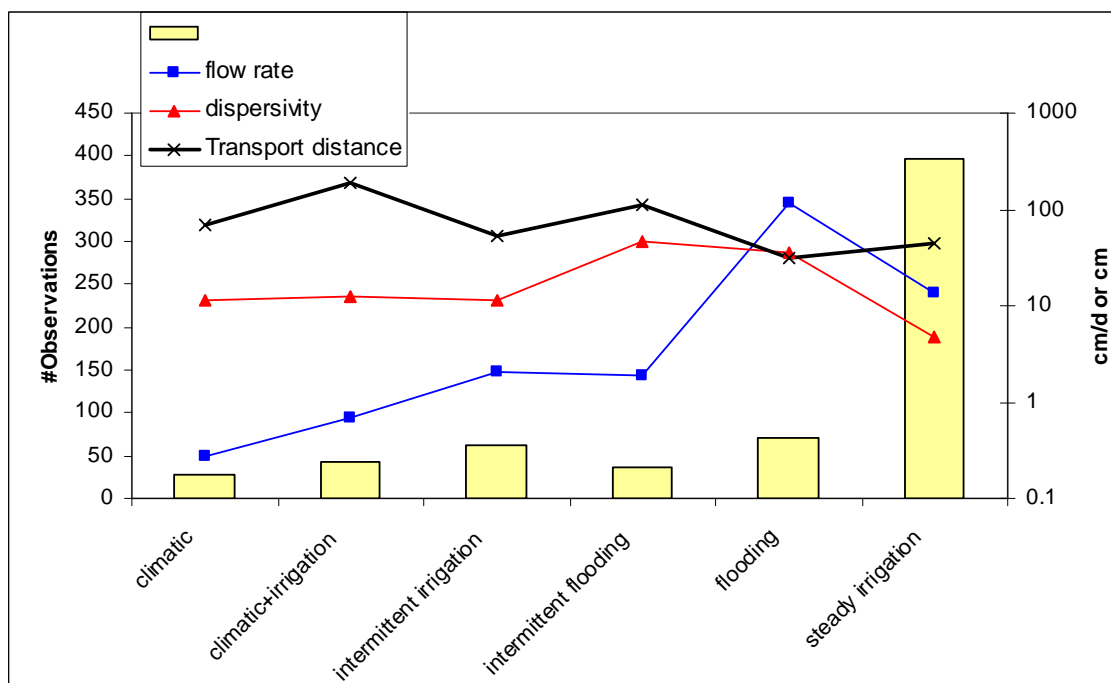
Figure A16-2. Number of observations (bars), mean flow rate (blue line), and mean dispersivity in the flow boundary condition classes.
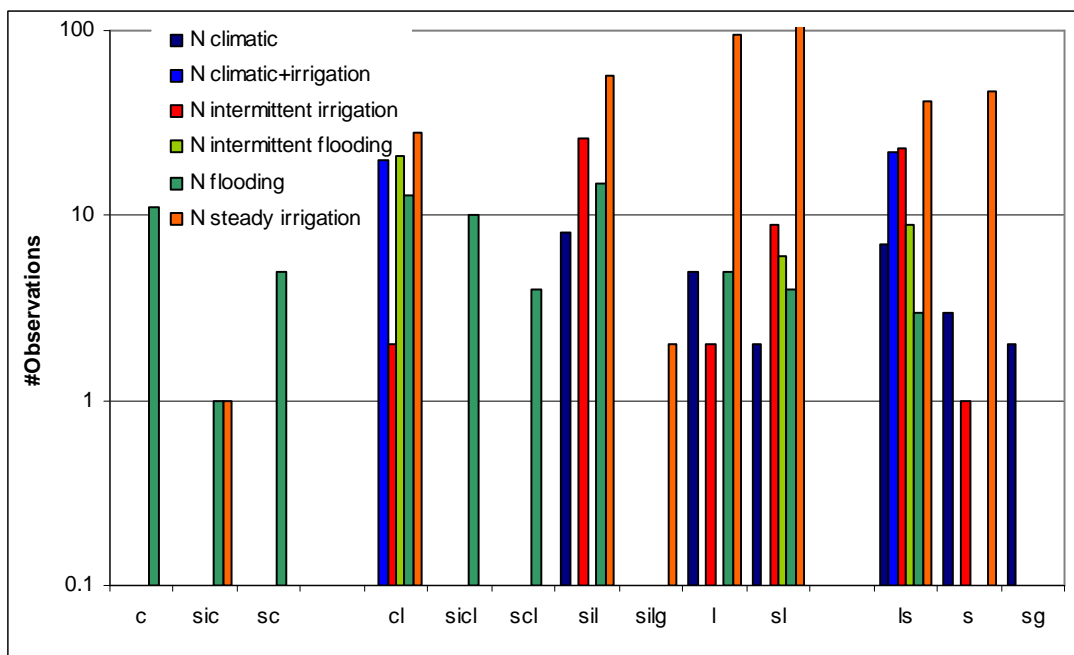
Figure A16-3. Number of observation in different soil texture classes (c:clay, sic: silty clay, sc: sandy clay, cl: clay loam, sicl: silty clay loam, scl: sandy clay loam, sil: silt loam, silg: silt loam gravel, l: loam, sl: sandy loam, ls: loamy sand, s: sand, sg: sandy gravel) and flow boundary condition classes.

With increasing scale of the leaching experiment, the average transport distance increases whereas the flow rate decreases (Figure A16-1). The effect of the experimental scale on the dispersivity length can therefore not be derived without considering the flow rate and transport distance. For both continuous and intermittent flooding boundary conditions, the mean dispersivity was considerably larger than for the other flow boundary conditions (Figure A16-2). The average flow rate was the highest for the continuous flooding boundary condition. The flow boundary condition seems to have a larger impact on the mean dispersivity length than the mean flow rate. For steady state irrigation, the mean flow rate was the second highest whereas the mean dispersivity was the smallest. For the intermittent flooding flow boundary condition, the mean dispersivity was the largest whereas the mean flow rate was similar to that for an intermittent irrigation under unsaturated flow conditions. As shown in Figure A16-3, most experiments in the clayey soils (c, sic, sc, cl, and scl) were carried out under saturated flow conditions. An examination of the combinations between soil texture and flow condition class (Figure A16-3) shows that in the clayey soils (c, sic, sc, cl, sicl, and scl) most experiments were carried out under saturated flow conditions. Experiments under climatic boundary conditions were mainly carried in coarser textured soils. To investigate the effect of soil texture on dispersivity, experiments that were carried out using flooding boundary conditions need to be excluded because of the effect of flooding

boundary conditions on the average dispersivity (Figure A16-2). This leads to a reduction of data available for the finer textured soils. Therefore, the soil texture classes were grouped into two classes: a 'coarse' texture class that lumps the sand, loamy sand and sandy loam classes and a 'fine' texture class lumping the other texture classes. Experiments that were carried out soils with a large stone content (texture classes sg and silg) were excluded because they were not considered to be relevant for agricultural use.

Effect of experimental factors on dispersivity

Although flow rate, J_w, and transport distance are continuous variables, their effect on the dispersivity length was investigated through flow rate and transport distance classes. For the flow rate, four classes were defined: flow rates smaller than 1 cm/d, between 1 cm/d and 10 cm/d, and larger than 10 cm/d. The experiments that were carried out using flooding boundary conditions were grouped in a separate flow class. If available, the effective flow rate was used to determine the flow rate class. Most of the experiments that were carried out under climatic conditions without irrigation or climatic conditions with intermittent irrigation were grouped in the flow class with flow rates smaller than 1 cm/d. Exceptions were studies in which a large amount of water was infiltrated during a short time (rainfall events of more than 100 mm d^{-1}). These studies fell into the class with flow rates larger than 10 cm/d.

For the transport distances, three classes were defined: studies with a transport distance smaller than or equal to 30 cm, between 31 cm and 80 cm and between 81 and 200 cm. The first class contains all soil core scale experiments and is relevant for the transport through the upper soil layer or plough layer where pesticide degradation and sorption are the largest. The last class is representative for transport experiments with a similar transport distance as the depth where the pesticide concentrations in the soil need to be defined, i.e. 100 cm.

In order to give the same weight to experiments where dispersivities were determined for several travel distances (e.g. in a soil column or a field plot), the data entries in a travel distance class that correspond to the same experiment or experiment number were averaged and further treated as a single entry.

Flow rate

In Figure A16-4, the distribution of dispersivities in the different flow rate and experimental scale classes are shown for two transport distance classes.
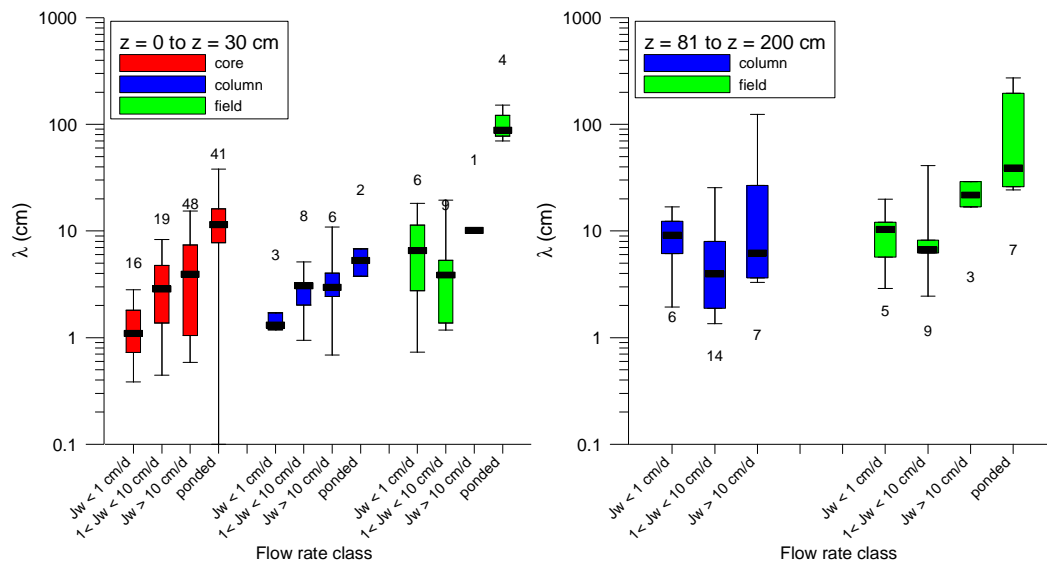
Figure A16-4. Effect of flow rate class and scale of the experiment on the dispersivity length for two transport distance classes. The boxes span the 25% and 75% percentiles, the thick black line is the median, and the 0% and 90% percentiles correspond with the extremities of the vertical bars. The numbers above or below the boxes correspond with the number of observations in the class.

Dispersivities derived from experiments that were carried out using a flooding boundary condition were consistently larger than dispersivities that were derived from other experiments. For the 0-30 cm travel distance class, there is a clear increase of dispersivity length with increasing flow rate in the core and column scale experiments. This increase is not seen in the field scale experiments or for the experiments in the 81-200 cm travel distance class.

Since surface flooding is not relevant for non irrigated and agriculturally used soils, experiments that were carried out by flooding or ponding the soil surface or saturating the soil columns were excluded. However, for the scenarios including irrigation, the dispersivity lengths derived for flooding boundary conditions or saturated soil columns might be considered when furrow or flood irrigation is used.

Except for those studies that were carried out under climatic boundary conditions without additional irrigation, all leaching studies are carried out under artificial boundary conditions. In order to reduce the duration of the leaching experiment, the average flow rate in leaching experiments is mostly considerably larger than under natural boundary conditions. On the other hand, rainfall and soil water flow are highly dynamic processes with high rainfall or flow intensities occurring during only a short time period and long intermittent periods without rainfall or large downward vertical flow. Therefore, close to the soil surface vertical

movement occurs during relatively short pulses with a high flow rate, which become sensibly buffered with depth, depending on the hydraulic buffer capacity of the soil. For the meteorological station in Jülich (Germany), Table A16-1 provides the percentiles of effective precipitation rates (based on a record of 20 years of hourly rainfall data)

Table A16-1. Percentiles of rainfall intensities for the meteorological station in Jülich (Germany).

Percentile	Rainfall intensity (cm/d)
Max	51.12
99	30.72
95	18.096
90	13.2
75	6.96
50 (Median)	3.6
25	1.68
10	0.72
5	0.48
1	0.24

The x% percentile represents the intensity which is larger than the rainfall intensity of x% of the total amount of precipitation.

According to Table A16-1, 10 % of the total yearly precipitation occurs with an intensity larger than 13.2 cm d^{-1} whereas half of the total yearly precipitation occurs with an intensity larger than 3.6 cm d^{-1}. This is more than a factor of ten larger than the total yearly precipitation divided by the numbers of days in a year, which corresponds with the yearly averaged infiltration rate at the soil surface. From that perspective, leaching experiments carried out using a flow rate of 10 cm d^{-1} may also be realistic for natural boundary conditions.

In order to exclude large dispersivities resulting from high irrigation and flow rates, only experiments with a flow rate smaller than 10 cm d^{-1} were retained for further analysis. Putting the maximal flow rate threshold lower did not result in significantly different dispersivity distributions.

Transport distance
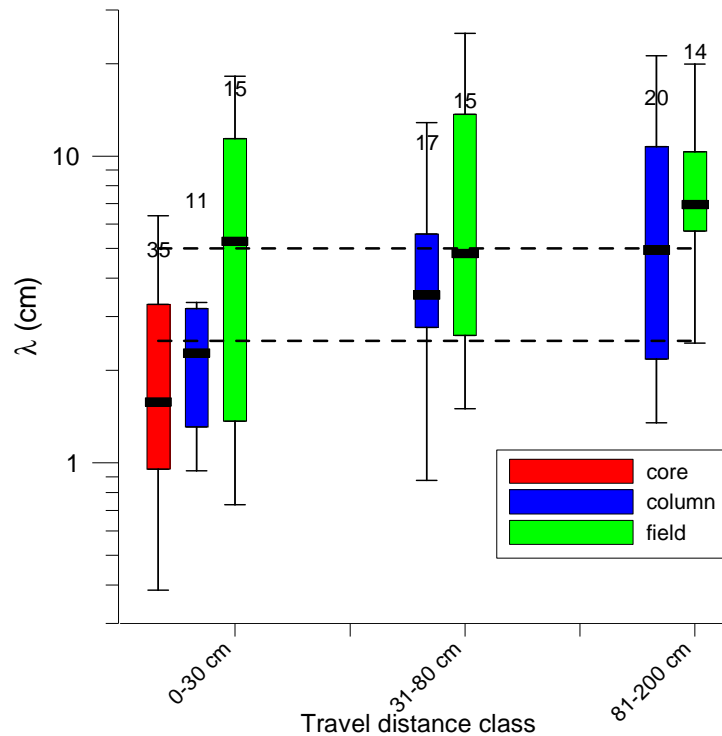
Figure A16-5. Effect of transport distance and scale of the experiment on the dispersivity. The boxes span the 25% and 75% percentiles, the thick black line is the median, and the 0% and 90% percentiles correspond with the extremities of the vertical bars. The numbers above the boxes correspond with the number of observations in the class. The dashed lines represent the dispersivity of 2.5 and 5 cm currently used in the FOCUS ground water scenarios.

Figure A16-5 illustrates that both the transport distance and the lateral scale of transport experiment has an impact on dispersivity length. Generally, the dispersivity length increases when the lateral scale of the experiment increases. Therefore, field scale experiments are expected to be more representative for the dispersion process under real conditions than experiments in soil columns or lysimeters that reduce lateral redistribution of water flow, and hence the dispersion process. However, the difference between field and column scale experiments is smaller for larger travel distances where the two distributions tend to converge. Furthermore, solute fluxes can be measured in a column experiment but not in a field experiment. In field experiments, concentrations are measured locally at a number of points and the actually sampled area is only a small fraction of the total cross sectional area of the field plot and may be even smaller than the area of a soil column or lysimeter. On the basis of these considerations, field and column scale experiments are considered to be of equal relevance.

The column scale experiments clearly show an increase of dispersivity with transport distance. For the field scale experiments, the dispersivity distribution in the 0-30 cm travel distance class is similar to that in the 31-80 cm class. For a travel distance of 100 cm, a dispersivity of 5 cm as used in the pesticide leaching calculations by the PEARL model is clearly in better agreement with the median of the experimentally determined dispersivities than the dispersivity of 2.5 cm which is used in the PRZM and PELMO calculations and which represents roughly the 25% percentile of the dispersivity distribution. The 2.5 cm dispersivity is more representative for the median of the dispersivity distributions in the core and column scale experiments for the 0-30 cm transport distance class. However, considering the field scale experiments, the 5 cm dispersivity seems to be a better choice also for the 0-30 cm transport distance class.

Texture
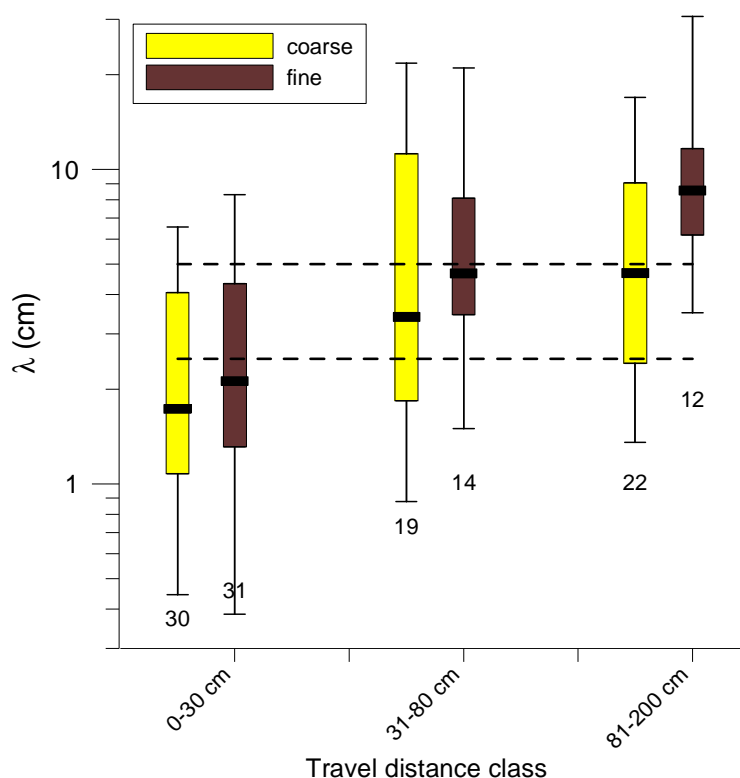
Figure A16-6. Effect of transport distance and soil texture class on the dispersivity. The boxes span the 25% and 75% percentiles, the thick black line is the median, and the 0% and 90% percentiles correspond with the extremities of the vertical bars. The numbers below the boxes correspond with the number of observations in the class. The dashed lines represent the dispersivity of 2.5 and 5 cm currently used in the FOCUS ground water scenarios.

Figure A16-6 suggests that dispersivities tend to be larger in finer than in coarser textured soils. But, the 5 cm dispersivity length is also more relevant for the coarser textured soils

486

and the 81-200 cm distance class. The fact that pesticide leaching is sensitive to the dispersivity, which tends to be larger in finer textured soils, raises the question whether coarser textured soils represent a worst case.

Variability of dispersivity values

The box plots in Figures A16-4 to A16-6 clearly illustrate that there is a large variability of the experimentally determined dispersivity values that is not explained by experimental factors. The dispersivity distributions are positively skewed and a logarithmic scale was used for the vertical axis of the plots. For positively skewed distributions, the arithmetic average is considerably larger than the median value or 50 % percentile and cannot be related directly to a percentile of the distribution. As discussed above, the 5 cm dispersivity used in the PEARL simulations corresponds with the median of the dispersivity distributions for the 31-80 cm and 81-200 cm travel distance classes whereas the 2.5 cm dispersivity corresponds with the median of the 0-30 cm travel distance class. However, can a median value be used in a scenario which is intended to represent a worst-case condition? If the 75% percentile is considered to be relevant for a worst case condition, then based on the distribution of experimentally determined dispersivities, a dispersivity of 10 cm should be used.

Implications of an increase of dispersivity with transport distance for the prediction of pesticide fate in soils with vertically varying sorption and degradation parameters.

The dispersivity for a certain transport distance was derived by fitting the solution of a 1-D convection dispersion model in a 'hydrodynamically' homogeneous soil profile, i.e. assuming a constant water content and constant dispersivity with depth, to a breakthrough curve or a concentration depth profile. The transport distance corresponds with the observation depth of the breakthrough curve or the location of the centre of mass of the concentration profile. The assumed 'hydrodynamically' homogeneous soil profile with depth independent parameters must therefore be interpreted as an equivalent model of the real soil profile in which the breakthrough of an inert tracer at the transport distance corresponds with that in the real soil profile. But, since λ depends on the transport distance (Figure A16-5), concentrations that are predicted in the equivalent 'hydrodynamically' homogeneous soil profile at other depths than the transport distance deviate from the concentrations in the real soil profile. These deviations introduce errors when depth dependent processes are introduced in the equivalent 'hydrodynamically' homogeneous soil profile. In the FOCUS scenarios, different decay rates and sorption coefficients are assumed in different soil layers. For the decay rate, three soil layers are considered: the 0-0.3m, 0.3-0.6 m and 0.6-1.0 soil layers. The decay rate in the deeper soil layers is a factor of the decay rate in the top layer:

0.5 for the 0.3-0.6 m and 0.3 for the 0.6-1.0 m layer. The sorption coefficient in the different soil layers is related to the organic carbon content.

The error on the leached mass fraction resulting from assuming a hydrodynamically homogeneous soil profile is assessed by comparing predictions in a hydrodynamically homogeneous soil profile with those in a profile with increasing dispersivity with travel distance. Two different models that represent a soil profile in which the dispersivity increases with depth are considered.

The first is a 'layered convection dispersion model'. In this model, the soil is divided into several layers and for each layer a different dispersivity is defined. For substances that undergo linear reactions (i.e. linear sorption isotherms and first-order decay rates) the transport in this hydrodynamically layered soil can be predicted using transfer functions. The breakthrough at the bottom of the nth layer is predicted by a convolution of the input concentrations at the top of that soil layer, $C_{in}(z_{n-1};t)$, with a transfer function, $f(\Delta z_n, t)$:

$$C(z_n,t) = \int_0^t C_{in}(z_{n-1};t-\tau) f(\Delta z_n, \tau) d\tau \tag{A16-3}$$

where z_n is the depth of the bottom of the nth soil layer, Δz_n is the thickness of the layer, and $f(\Delta z_n, t)$ is the transfer function in the nth layer.

For a convection dispersion equation with linear sorption and a first-order decay $f(\Delta z_n, t)$ is given by:

$$f(\Delta z_n, t) = \exp(-\mu_n t) \frac{\Delta z_n}{2\sqrt{\dfrac{\pi \lambda_n v_n t^3}{R_n}}} \exp\left(-\frac{\left(\Delta z_n - \dfrac{v_n t}{R}\right)^2}{4\lambda_n v_n t / R_n}\right) \tag{A16-4}$$

where μ_n (T^{-1}) is the first-order decay rate, v_n (L T^{-1}) is the pore water velocity, R_n the retardation coefficient, and λ_n (L) the dispersivity of the nth layer.

The retardation coefficient R_n is defined as:

$$R_n = 1 + \frac{\rho_b K_{oc} OC_n}{\theta} \tag{A16-5}$$

where ρ_b is the soil bulk density, K_{oc} the pesticide-organic carbon partitioning coefficient, OC_n the organic carbon weight fraction in the nth soil layer and θ the volumetric soil water content.

The dispersivity of the nth layer is derived from the dispersivities in the overlaying layers, λ_i, and the dispersivity that was derived for a travel distance z_n assuming a 'hydrodynamically' homogeneous soil profile, $\lambda(z_n)$. This is done by matching the variances of particle travel times to depth z_n, $var(t;z_n)$ that are predicted in the layered and in the 'hydrodynamically' homogeneous soil profiles. For the layered soil profile, $var(t;z_n)$ is related to the variance of travel times through the soil layers, $var(t;\Delta z_i)$ as:

$$\text{var}(t; z_n) = \sum_{i=1}^{n} \text{var}(t; \Delta z_i) \tag{A16-6}$$

Using the relation between the dispersivity in a 'hydrodynamically' homogeneous soil and $var(t;z)$:

$$\text{var}(t; z) = \frac{2\lambda z}{v^2} \tag{A16-7}$$

the dispersivity of soil layer n, λ_n, is derived from the dispersivities in the overlaying soil layers and the dispersivity in a 'hydrodynamically' homogeneous soil profile for a travel distance z_n, $\lambda(z_n)$, as:

$$\lambda_n = \frac{z_n \lambda(z_n)}{\Delta z_n} - \sum_{i=1}^{n-1} \frac{\Delta z_i \lambda_i}{\Delta z_n} \tag{A16-8}$$

The layered convection dispersion model postulates that there is no correlation of the travel times of given particle through different layers so that the variance of particle arrival times at the bottom of a certain layer can be written as the sum of the travel time variances through the overlaying layers (Equation A16-6). The fact that the dispersivity increases with travel distance is however contradictory to this assumption since it is an indication that velocities along the trajectory of a single particle are correlated, which implies that the travel time of a particle through a certain layer is correlated with its travel time through another layer.

The second model, the 'stream tube model' with vertically varying sorption and degradation parameters, assumes that a solute particle keeps a constant velocity along its trajectory through the soil. Due to this correlation of particle velocities, the travel time variance increases quadratically with travel distance. This corresponds to a linear increase of the dispersivity length with travel distance. Using a stream tube model, the mass faction, *M(z)* of a substance that leaches at a certain depth is given as:

$$M(z) = \int_0^\infty \exp\left(-\frac{\mu_{tot}}{R_{tot}}t\right)\frac{1}{\sqrt{2\pi\sigma t}}\exp\left(-\frac{\left(\ln\left(\frac{t}{R_{tot}}\right)-\mu\right)^2}{2\sigma^2}\right)dt \qquad \text{(A16-9)}$$

where $\mu_{tot} = \dfrac{\sum_i \mu_i R_i \Delta z_i}{\sum_i \Delta z_i}$ ($\mu_i = \ln(2)/\text{DegT50}_i$), $R_{tot} = \dfrac{\sum_i R_i \Delta z_i}{\sum_i \Delta z_i}$ $\left(R_i = 1 + \rho_b \dfrac{K_{oc}OC_i}{\theta}\right)$, and σ^2

and μ are the variance and mean of the $\log_e$ transformed travel time distribution.

The parameters σ^2 and μ are related to the mean particle velocity, v, and the dispersivity length $\lambda(z)$ through:

$$\sigma^2 = \ln\left(2\frac{\lambda(z)}{z}+1\right) \qquad \text{(A16-10)}$$

$$\mu = \ln\left(\frac{z}{v}\right) - \frac{\sigma^2}{2} \qquad \text{(A16-11)}$$

In order to assess the effect of the model choice on the leached mass fraction, leached mass fractions were calculated for a set of dummy substances in a soil profile consisting of three layers: 0-30 cm, 30-60 cm, and 60-100 cm. The DegT50 of the dummy substances in the top layer ranges from 5 to 200 d and the K_{oc} from 10-200 mL g^{-1}. The hydrodynamic parameterization of the soil profile is based on the median values of the dispersivity distributions. The models considered are: the hydrodynamically homogeneous soil profile, the layered convection dispersion model, and the stream tube model. The dispersivity is assumed to increase linearly with the travel distance and that the dispersivity for a travel distance of 100 cm equals 6 cm. In Table A16-2 the soil parameters are given:

Table A16-2. Dispersivity lengths of the hydrodynamically homogeneous soil profile λ(z), of the different soil layers, λ$_i$, organic carbon content, OC, DegT50, volumetric water content, θ, and bulk density, ρ$_b$.

Depth	λ(z)	λ$_i$	OC	DegT50/DegT50$_{top}$	θ	ρ$_b$
cm			g g^{-1}			g mL^{-1}
30	1.8	1.8	0.02	1	0.3	1.4
60	3.6	5.4	0.01	2	0.3	1.4
100	6	9.6	0.0067	3.33	0.3	1.4

A percolation rate of 300 mm a^{-1} was assumed, resulting in a pore water velocity of 1 m a^{-1}.

Figure A16-7 provides a schematic representation of the three models and their parameterization. Figure A16-8 shows how the parameterization of the dispersivity lengths compares with the dispersivity distributions for different travel distances.
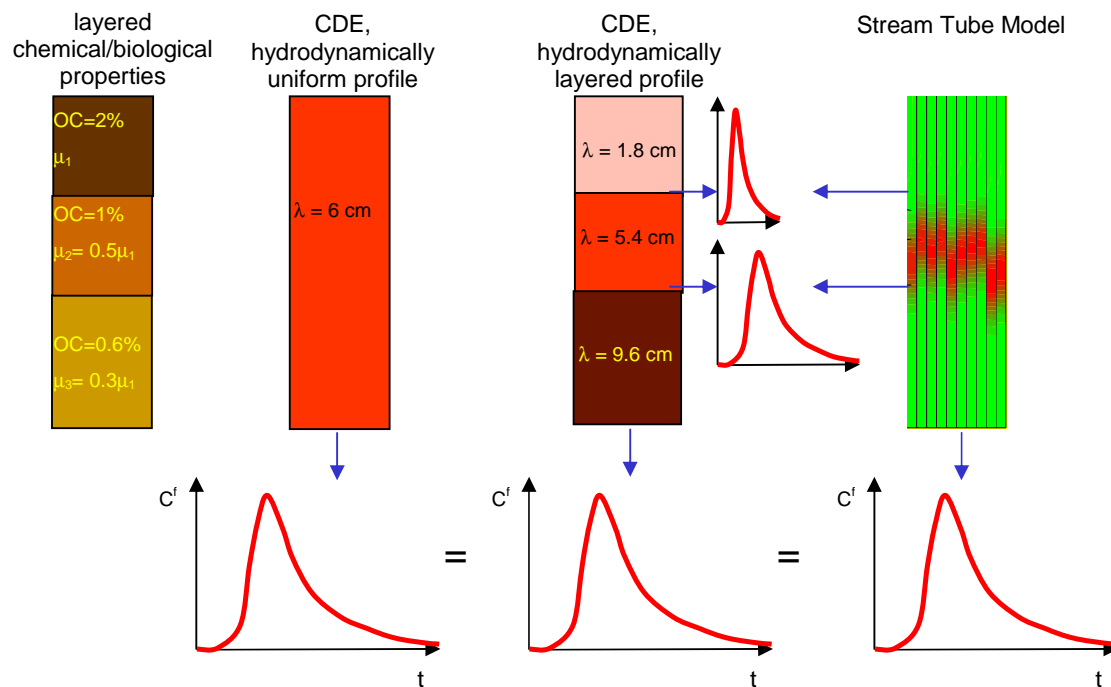
Figure A16-7. Schematic representation of the three models and the prediction of the breakthrough of an inert tracer at the bottom of soil profile and at the bottom of the soil layers.
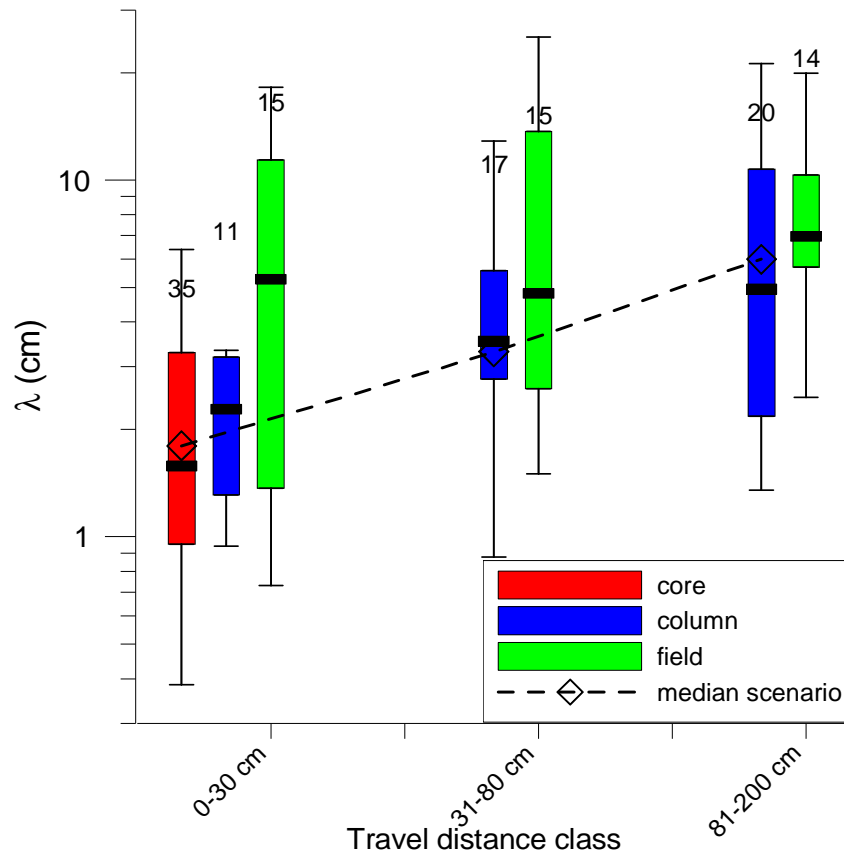
Figure A16-8. Parameterization of the dispersivity lengths in comparison with the dispersivity distributions for different travel distance classes and experimental scales.

The three models predict the same breakthrough of an inert tracer at 1 m depth in the soil profile. Furthermore, the layered convective dispersive and the stream tube model predict the same breakthrough of an inter tracer at 30 and 60 cm depth, which corresponds with the bottom of the first and second soil layer, within the soil profile. For comparison, a fourth model in a hydrodynamically uniform soil profile with a small dispersivity length (λ = 1.8 cm) was considered. This model predicts the same breakthrough of an inert tracer at the bottom of the first soil layer (30 cm) as the stream tube and the layered CDE models. Figure A16-9 shows the breakthrough curves of two substances, one with relatively low and one with a relatively high leaching potential, that are predicted by the four different models at three different depths: 0.3, 0.6 and 1.0 m. These depths correspond with the boundaries of the layers with different sorption and decay rate parameters. An application dose of 1kg /ha was assumed.
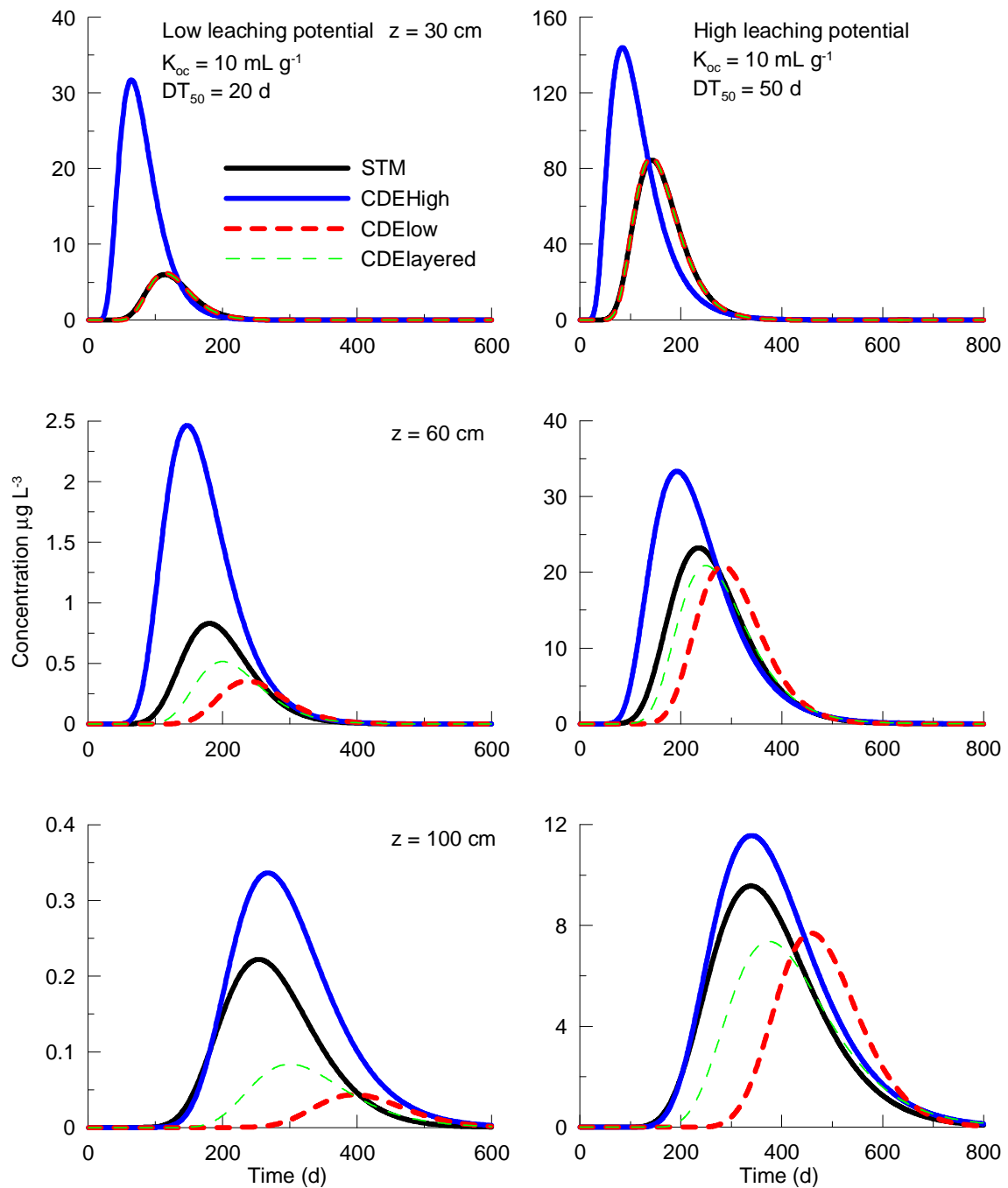
Figure A16-9. Prediction of breakthrough curves of a substance with a low leaching potential (left graphs) and a substance with a high leaching potential (right graphs) at three different depths by three different models: stream tube model (STM), hydrodynamically uniform CDE model (CDEHigh), and layered CDE model, that predict the same breakthrough of an inert tracer at 100 cm depth, and by a hydrodynamically uniform CDE with a small dispersivity length (CDElow).

Figure A16-9 shows that:

1. The highest peak concentrations are predicted by the hydrodynamically uniform CDE with the high dispersivity.
2. The three models that predict the same breakthrough of an inert tracer at 100 cm (i.e. the hydrodynamically uniform CDE with high dispersivity, the stream tube model, and the layered CDE model) do not predict the same breakthrough of a reactive tracer at 100 cm depth. The differences are in relative terms (note the different scales of the y-axes) much larger for the substance with the low leaching potential.
3. The models that predict the same breakthrough of an inert tracer at 30 cm depth (i.e. the CDE with a low dispersivity, the layered CDE and the STM) also predict the same BTC of the reactive substances at 30 cm depth.
4. The two models that predict the same breakthrough of an inert tracer at the layer boundaries within the profile (i.e. the layered CDE and the STM) do not predict the same breakthrough of the reactive substances at 60 and 100 m depth.

Point 1 is counter intuitive since a high dispersivity implies high dispersive fluxes that smooth out or decrease concentration peaks. A higher dispersive flux also implies that a larger fraction of the surface applied mass can be rapidly transferred through the soil column. The fraction that is rapidly transferred has less time or opportunity to decay. The ratio of the mass of a decaying substance compared with that of a non decaying tracer that reaches a certain depth is close to 1 for small transfer times but decreases with increasing transfer time. This is illustrated in Figure A16-10 where breakthrough curves of decaying and non-decaying substances at 100 cm depth are plotted on a logarithmic scale. When decay is relatively fast, i.e. the ratio between the decaying and non-decaying substance concentrations decreases rapidly in the time period between the first significant breakthrough of the non-reactive substance and the breakthrough of the concentration peak, higher peak concentrations of the decaying substance may be predicted for larger dispersivities. However, when decay is relatively slow and the ratio between decaying and non-decaying substance concentrations decreases slower between the first significant breakthrough and the arrival of the peak concentration, smaller peak concentrations of a decaying may be predicted for a higher dispersivity than for a lower dispersivity. This explains why the layered CDE predicts a smaller peak concentration at 100 cm of the substance with the high leaching potential than the CDE model with a small dispersivity.
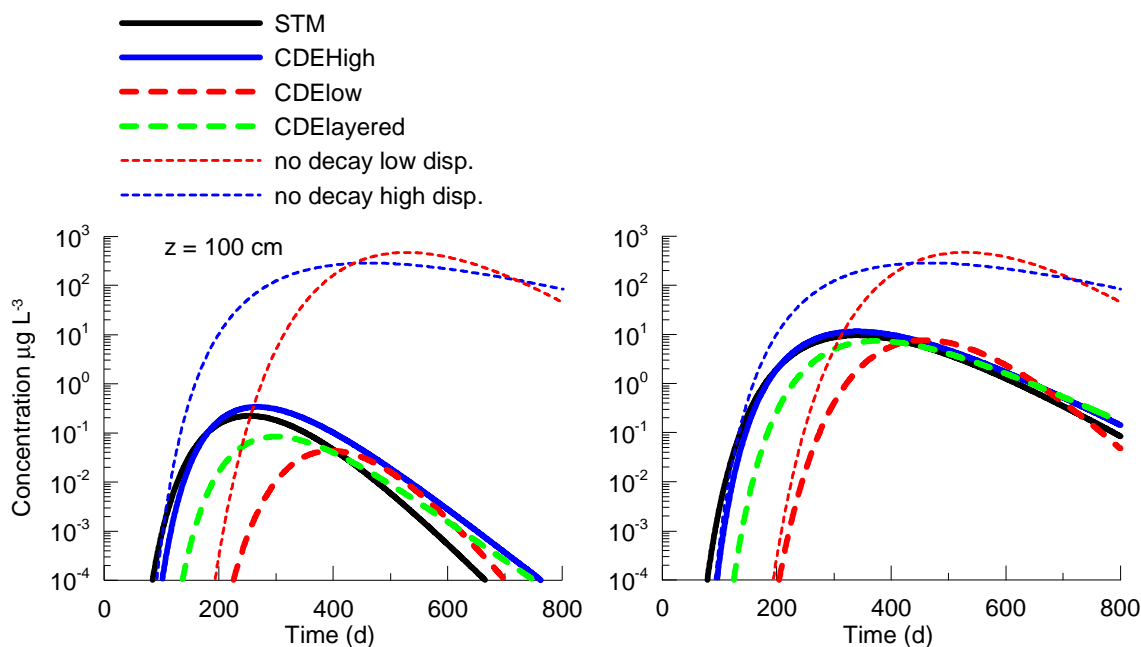
Figure A16-10. Same as Figure A16-9 but concentration are plotted on a logarithmic scale. Thin dashed lines are predictions for a substance that does not decay.

Point 2 implies that for the prediction of a reactive substance undergoing decay, differences in dispersion fluxes or dispersion constants at different depths in the soil profile must be considered, especially for solutes with a low leaching potential. However, point 3 demonstrates that for constant decay rate and sorption parameters with depth (i.e. in the upper 30 cm of the considered soil profile), the prediction of the breakthrough curve of a decaying substance at a certain depth (i.e. at 30 cm) is the same for models that predict the same breakthrough of an inert tracer at that depth, irrespective of the prediction of breakthrough curves by these models at other depths in the profile. If decay rate and sorption parameters vary with depth, then different dispersive fluxes at different depths in the soil profile imply different transfer time distributions and different leached mass fractions through the different layers. Therefore, models that assume different dispersive fluxes through different soil layers predict different breakthrough curves of a decaying substance at the bottom of the soil profile even when these models predict the same breakthrough of an inert tracer at the bottom of the profile.

Point 4 implies that besides the transfer time variability through the different soil layers, also the correlation of transfer times of individual solute particles through two different soil layers plays a role. The stream tube and layered CDE models predict the same breakthrough of an inert tracer at the layer boundaries in the soil profile yet different breakthrough curves of the

495

reactive substances. In the stream tube model, the variance of travel times through soil layers is the same for layers with the same thickness and the model assumes that transfer times of a particle in two different layers are perfectly correlated. In the layered CDE model, the transfer times of a particle in two different layers are not correlated and the loss of travel time correlation is compensated by a higher transit time variance or higher dispersivity in the deeper soil layer. However, this compensation is based on transit time variances of an inert tracer. For a substance that is undergoing decay, only the fraction of the applied mass that is rapidly transferred through the first layer reaches the surface of the second layer. In the stream tube model, this fraction is also rapidly transferred through the second layer since a perfect correlation of transfer times is assumed. In the layered CDE model, the transfer time of this fraction through the second layer is not correlated to its transfer time through the first layer so that it is transferred with an average velocity through the second layer. Therefore, the residence time and the opportunity for decay in the second layer of the fraction of the applied mass that leaches through the first layer and reaches the second layer are smaller for the STM than for the layered CDE model. This explains why the stream tube model predicts more leaching at the bottom of the second and third soil layers than the layered CDE model.

Figure A16-11 shows the predicted leached mass fractions at 1 m depth plotted versus the predicted leached mass fraction by the stream tube model. Despite the same inert tracer breakthrough is predicted at 1 m depth by the three models, the predicted leached mass fractions of a substance that undergoes sorption and decay is quite different and the relative differences between the model predictions increase with decreasing leaching potential of the substances.
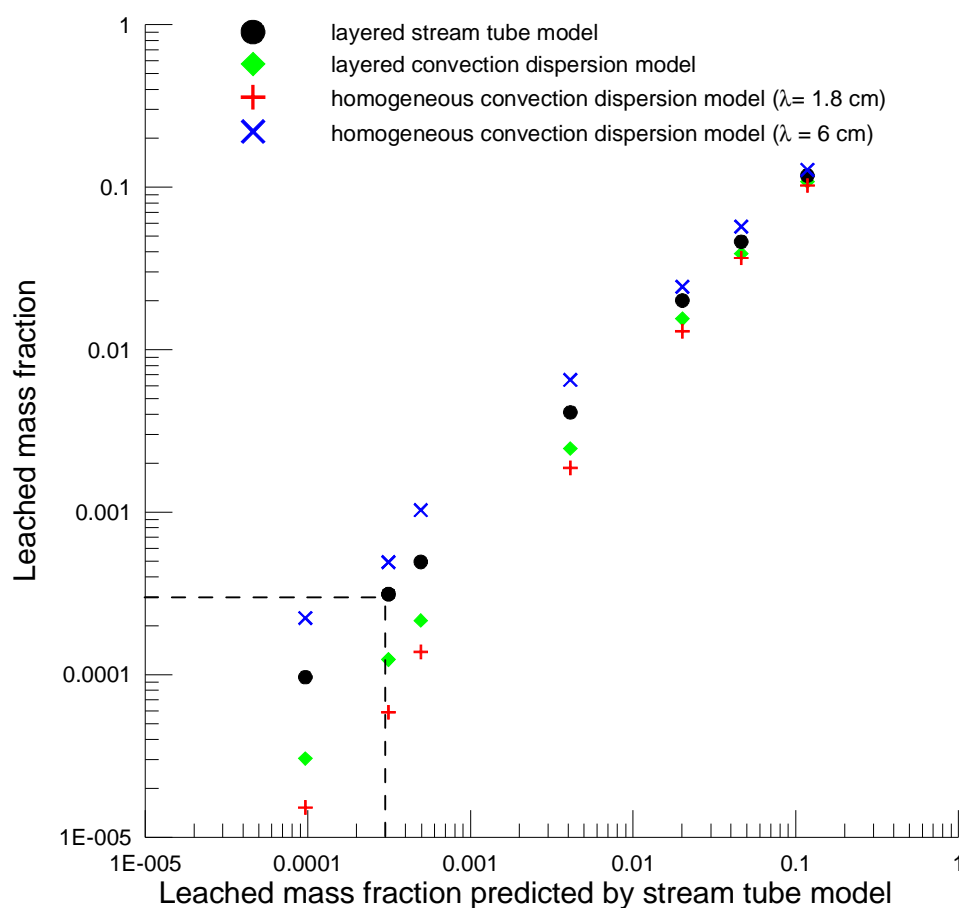
Figure A16-11. Predicted leached mass fraction at 1 m depth in a layered soil profile by a stream tube model versus the predicted leached mass fraction by a convection dispersion model for a high and a low uniform dispersivity, and for a depth dependent dispersivity. Dashed lines represent the maximal leached mass fraction for a yearly averaged concentration < 0.1 μg L^{-1}, an application dose of 1 kg ha^{-1}, and a deep percolation of 300 mm a^{-1}.

Leached mass fractions predicted by the layered convection dispersion model are closer to those predicted in a hydrodynamically uniform soil profile using a dispersivity length which is relevant for the transfer through the first soil layer. The stream tube model predictions better agree with those predicted in a hydrodynamically uniform soil profile using a dispersivity length which is relevant for transport through the entire soil profile.

The differences in predicted leached mass fractions by the layered CDE and the stream tube models illustrate a fundamental problem of using models that are parameterized on the basis of inert tracer experiments to predict the behaviour of reactive substances in a soil. Besides knowledge about inert tracer breakthrough at various depths within a soil profile, the mechanisms that explain the observed inert tracer transport must be correctly represented in a mechanistic model in order to predict the fate of other substances correctly. The stream

tube model provides a mechanistic explanation of the observed increase of dispersivity with travel distance by postulating a correlation of velocities along the trajectories of individual particles. Therefore, a correlation of particle velocities across layer boundaries may be assumed to better represent the transport mechanisms than a convection dispersion model which postulates no correlation. On the other hand, the lower dispersivity in the upper soil layer may be explained by soil homogenization due to tillage and the higher dispersivity in the deep soil layer may reflect the larger heterogeneity of the natural soil. Whether this soil homogenization reduces the correlation between particle transit times through the top and the subsoil layers and whether a layered CDE better describes the transport process for this situation requires further investigation

If a convective dispersive model is to be used for predictions of pesticide fate and leaching, then a parameterization of the convective dispersive model assuming a hydrodynamically homogeneous soil profile and using a dispersivity length which is relevant for the transfer through the entire soil profile seems to be a conservative choice. However, note that the degree of conservatism depends on the vertical layering of the decay and sorption constants. The divergence of the predicted leached mass fraction by the different models in Figure A16-11 depends on the profile of the normalized decay and sorption parameters (normalized with respect to the decay and sorption parameters at the soil surface). If the sorption and decay constants do not change with depth, then predictions by the stream tube model, the hydrodynamically homogeneous CDE model with high dispersivity length and the layered CDE model converge whereas the hydrodynamically homogeneous CDE model with a low dispersivity length underestimates the leached mass fraction. If there is no decay below the first soil layer (i.e. below 30-cm), then the layered CDE model and the homogeneous CDE model with a low dispersivity length predict the same leached mass fraction as the stream tube model whereas the high dispersivity CDE model overestimates the leached mass fraction.

Note also that the above discussion applies only to substances of which the sorption isotherm is linear. For non-linearly sorbing substances, the convective dispersive model is less conservative than a stream tube model in soil profiles with vertically constant decay and sorption parameters. This is a result of the lower dilution of local concentrations that are predicted by a stream tube model. Due to the non-linearity of the sorption isotherm, higher local concentrations in individual stream tubes propagate faster through the soil than the horizontally lumped concentrations, which are lower, that are predicted by the convection dispersion model.

Plausibility checks for layered CDE and stream tube models. Numerical simulations of solute transport in heterogeneous flow fields

In the previous section, significant differences between the predictions of the leached mass fractions of a reactive substance by a stream tube model and a by a layered CDE model were observed. Both models reproduce the observed increase of dispersivity length with travel distance (Figure A16-5), but make different assumptions about the correlation of solute particle velocities across the layer boundaries. Since both models predict the same breakthrough of an inert tracer at the soil layer boundaries, information about inert tracer transport (on the basis of which the data base of dispersivity lengths was set up) cannot be used to discriminate which of both models best predicts the transport of decaying substances.

In order to validate both models, experimental data sets of breakthrough curves of inert and decaying tracers at various depths in combination with data on the change of decay and sorption rate parameters with depth would be required. Since such data sets are not available, we must rely on other representations of reality.

An argument in favour of the layered CDE model is that the top soil is homogenized by tillage. Therefore, a hypothesis might be that transport in the top soil is more homogeneous and characterized by a lower dispersivity length that transport in the subsoil. This hypothesis can be checked by looking at dispersivities observed in soil cores taken from different soil layers (Figure A16-12).
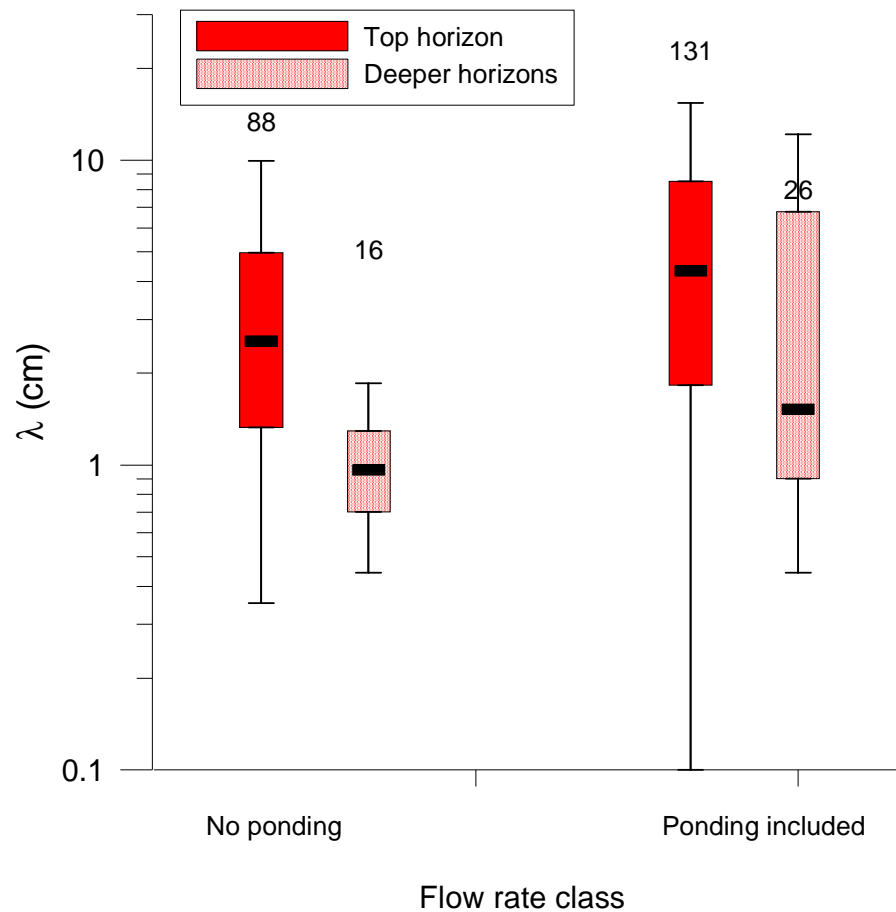
Figure A16-12. Distribution of dispersivities derived from core scale experiments in cores taken from the top soil (A-horizon) and from the subsoil (B and C-horizons). Distributions are shown for data sets excluding leaching experiments that were carried out in saturated soil columns (no-ponding) and data sets including these experiments (ponding included)

In general, the number of soil core experiments that were conducted in soil cores taken from the top soil outweighs the number of experiments in cores from the deeper soil layers. But, on the basis of the available data, it cannot be concluded that the dispersivity of a soil core taken from the subsoil is larger than that of a core from the top soil. Therefore, data from soil core leaching experiment do not support the use of a layered CDE, which presumes that the dispersivity in deeper soil layers is higher than in the top soil layer because the soil properties, with respect to solute dispersion, are in general different from those of the top soil layer.

The increase of dispersivity with increasing travel distance must therefore be attributed to a spatial variability and spatial correlation of water fluxes and soil hydraulic properties that are correlated over a distance in the same order of magnitude as the transport distance. If the

spatial correlation were not of the same order of magnitude as the transport distance, the dispersivity in soil cores taken from deeper soil cores should be much larger than the one from soil cores of the top soil to explain the increase of dispersivity with increasing travel distance.

Both the layered CDE and the STM make extreme assumptions about the spatial correlation of water fluxes in the soil profile. The assumption of no correlation in the layered CDE can not be maintained when considering dispersivities of soil cores taken from different soil layers. On the other hand, a perfect correlation of water fluxes through the soil profile would imply a linear increase of the dispersivity length with increasing travel distance. Figure A16-8 demonstrates that the increase of dispersivity with increasing travel distance tends to level off with increasing travel distance, which is a sign of an imperfect correlation of particle velocities along their trajectory through the entire soil profile. To investigate further which of both models can be used to predict transport in case of imperfectly correlated particle velocities, numerical experiments were carried out. In one-dimensional models, the spatial variability and correlation of water fluxes is not explicitly considered, but its effect on solute transport is lumped into the dispersion length. Therefore, numerical simulations that explicitly account for the spatial variability of hydraulic properties and water fluxes were used as surrogates for real experimental data. The spatial variability of the local water fluxes is in turn determined by the spatial variability of soil hydraulic properties, which can be characterized in a geostatistical framework by defining the mean value, the variance, and the correlation between values at different locations as a function of the separation between the two locations. In order to further investigate transport of a decaying substance in a layered soil profile (in terms of decay rate and sorption parameters), flow and transport were simulated in heterogeneous hydraulic conductivity fields. Since the correlation of particle velocities in layers with different decay and sorption parameters was shown to have an impact on the predicted leached mass fraction, two contrasting models of hydraulic conductivity fields were considered. The geostatistical parameters for both models were chosen so that dispersivities derived from simulated inert tracer transport were similar to the median values of the dispersivity distributions. The first model assumes a stationary distribution of the hydraulic conductivity, i.e. the geostatistical parameters, i.e. mean, variance and spatial correlation function, are constant in the soil profile. This assumption means that there is no soil layering with respect to the hydraulic properties and that soil hydraulic properties are correlated across the boundaries of soil layers with different sorption and decay parameters. But the spatial correlation of the hydraulic properties in the main flow direction was chosen to be 10 cm, which is a factor 10 smaller than the transport distance. Therefore, this model does not perfectly match with a stream tube model, which would presume a spatial correlation that is

much larger than the transport distance. In the second case, the soil profile is assumed to be made of two layers with different geostatistical parameters, with the top layer (0-30 cm) representing a plough layer and the deeper layer (30-100 cm) representing the subsoil. The spatial distributions of hydraulic properties in the two layers are assumed to be independent of each other, i.e. there is no correlation between the hydraulic properties across the layer boundary. In order to limit the complexity of the relations between the spatial variability of hydraulic soil properties and the dispersivity length, a water saturated soil profile was assumed. The geostatistical parameters of the hydraulic properties can be directly determined so that the dispersivity lengths and their dependence on the travel distance match the constraints. Fields of hydraulic properties that lead to similar flow fields and dispersivity lengths could also be defined for unsaturated flow conditions. But, since soil water pressure heads must be continuous across soil layer boundaries and since the unsaturated hydraulic conductivity depends in a strongly non-linear way on the soil water pressure, unsaturated hydraulic conductivities will be partly correlated across the soil layer boundaries through the water pressures, even when the hydraulic parameters are not correlated. Therefore, flow simulations under saturated conditions can be considered as an extreme case to investigate the effect of the correlation of hydraulic properties across layer boundaries on transport of a decaying substance and evaluate the opposing assumptions made in the stream tube and layered CDE model about the correlation of particle travel times in different soil layers.

In order to limit the numerical effort, simulations were carried out in 2-D conductivity fields. The 2-D approximation leads to quantitatively different relations between the geostatistical parameters of the hydraulic conductivity and the dispersivity then in the 3-D case. However, the effect of heterogeneity on transport is qualitatively the same in 2-D and 3-D flow fields.

The geostatistical parameters of the hydraulic conductivity distributions in models are given in Table A16-3.

Table A16-3. Geostatistical parameters: γ_1 and γ_2 are the correlation lengths of an exponential spatial correlation function and σ^2_f is the variance of the $\log_e$ transformed saturated hydraulic conductivity.

	γ_1 (cm)	γ_2 (cm)	σ^2_f
model 1	10	10	1
model 2: 0-30 cm depth	10	10	0.6
model 2: 30-100 cm depth	30	5	0.6

For each model, 20 representations a conductivity field of 200 cm width and 100 cm depth were generated and flow and transport were simulated in each representation. Three different substances were considered: an inert tracer, a substance with a low leaching potential and one with a high leaching potential. The parameters used for the transport simulations are given in Table A16-4.

Table A16-4. Volumetric water contents (θ), bulk density (ρ_b), organic carbon content (OC), K_{oc} value of the substance, and DegT50 values of the substances in the three different layers

Depth	θ	ρ_b	OC	K_{oc}	DegT50 slow	DegT50 fast
		gr mL^{-1}	g g^{-1}	mL g^{-1}	D	d
0-30 cm	0.5	1.5	0.02	50	23	5.8
30-60 cm	0.5	1.5	0.01	50	46	11.6
60 -90 cm	0.5	1.5	0.006	50	77	19.3

In Figure A16-13, an example of a generated stationary and a layered heterogeneous K-field are shown together with the simulated pore water velocity distributions. In the stationary and K field with an isotropic structure (i.e. horizontal and vertical correlation lengths are equal) a braided and tortuous network of regions with higher water fluxes develops. Because of the longer vertical correlation length of the hydraulic conductivity in the subsoil of the layered soil profile, the regions with high water fluxes are more vertical and similar to vertical 'stream tubes'. Despite the uncorrelated hydraulic conductivities across the layer boundary, the regions with higher water fluxes in the subsoil seem to be connected or to be 'fed' by high flow regions in the top layer.
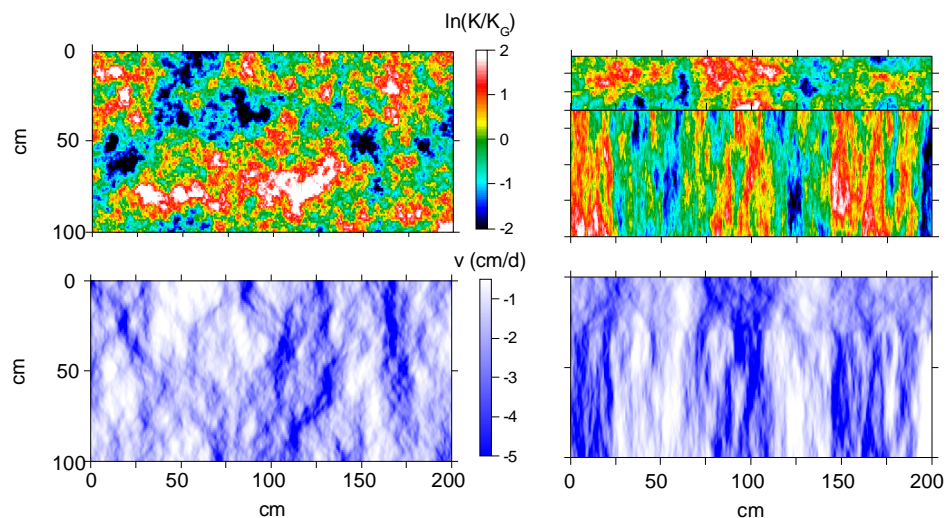
Figure A16-13. Representations of the hydraulic conductivity fields (top panels) and the simulated flow field (bottom panels) for the stationary (left panels) and layered (right panels) K-fields.

Dispersivity lengths and pore water velocities were derived for different transport distances by fitting the convection dispersion model to simulated flux weighted averaged breakthrough curves (i.e. local concentrations are weighted by the local water flux so that the averaged concentration is equal to the total solute flux divided by the total water flux) of the inert tracer.
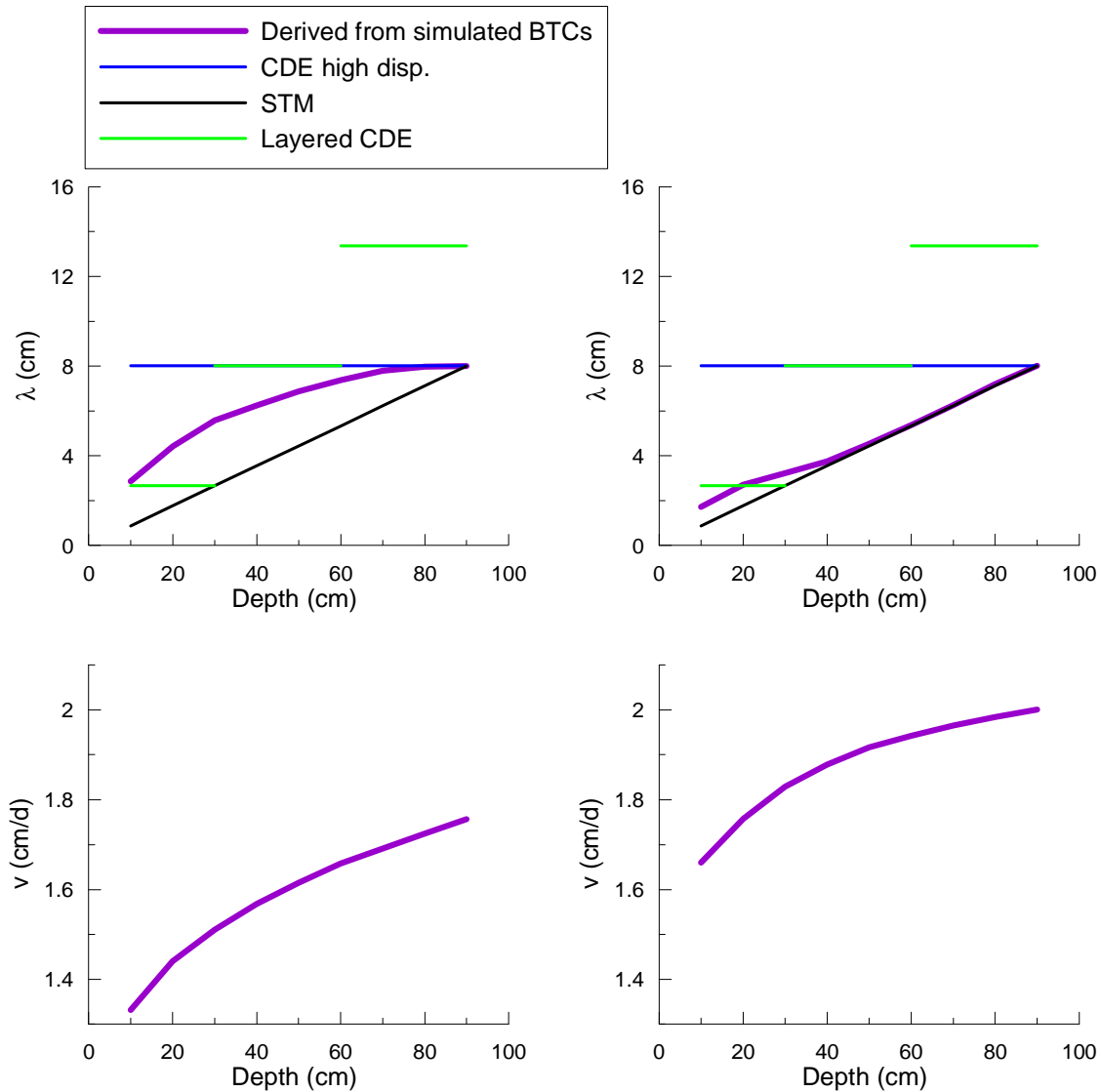
Figure A16-14. Dispersivity lengths (λ) (top panels) and pore water velocities (v) (bottom panels) derived from simulated flux weighted averaged BTCs at different depths in the stationary (left panels) and the layered heterogeneous K fields (right panels). Also dispersivity lengths used in the different 1-D models that predict the same breakthrough at 90 cm depth are shown.

The average particle velocity, which was derived from the simulated flux weighted averaged breakthrough curves, is smaller than the average pore water velocity (i.e. the average water flux divided by the volumetric water content, which is 2 cm d^{-1}), but increases with travel distance. This is a result of the solute application mode whereby an equal amount of solute mass is applied per unit area, irrespective of the local water flux (i.e. a uniform initial value problem). In heterogeneous flow fields, such an application mode leads to a smaller average particle velocity (which is for small travel distances equal to the harmonic average of the local pore water velocities) than the (arithmetic) average pore water velocity. Deeper in the soil

505

profile, solute mass is redistributed by lateral water fluxes and the mass that passes a unit area becomes proportional to the local water flux so that the average solute particle velocity approaches the arithmetic average of local pore water velocities. If the surface applied solute mass per unit area is proportional to the local water flux (i.e. a uniform boundary value problem), then the particle velocity does not change with travel distance in a heterogeneous flow field. In the 1-D transport models, the pore water velocity is constant with depth or travel distance. In order to make the predictions by the 1-D models and the predictions in the 2-D heterogeneous flow fields consistent, the simulations in the heterogeneous flow fields could be rerun for a uniform boundary value problem. Since this option is currently not available in the particle tracking code that we used, we implemented an additional retardation factor in the 1-D models so that the predicted inert tracer BTCs by the 1-D models at the boundaries between the three different layers match with the predictions in the heterogeneous flow fields.

For the chosen variability of the hydraulic conductivity fields, the dispersivity at 90 cm depth turned out to be 8 cm, which is larger than its first-order approximate estimate from the geostatistical parameters of the hydraulic conductivity field and than the median value of the dispersivity distribution. Since the objective of the numerical simulations is to compare the predictions of the three different 1-D models with simulations in heterogeneous flow fields that represent the process of solute dispersion in a more realistic way, the magnitude of the dispersivity as such is not so relevant, as long as the same value is used in the 1-D models.

As a result of the different structure of the heterogeneous K fields and corresponding flow fields (Figure A16-13), the change of dispersivity with travel distance is different in the stationary and layered heterogeneous K-fields. The rapid increase of dispersivity in the upper part of the stationary K-field is a result of the larger variability of the hydraulic conductivity (see Table A16-3). At a depth of 30 cm (the bottom of the first layer), the dispersivity already reached a value of 5.6 cm in the stationary K-field, which is considerably larger than the dispersivity in the layered K-field, 3.2 cm, and the dispersivity of the first soil layer, 2.7 cm in the layered CDE and STM models. In the stationary K-field, the rate of increase of the dispersivity with depth clearly levels off deeper in the soil profile whereas in the layered K-profile, the dispersivity increases nearly linearly with depth. This is a result of the larger spatial correlation in the vertical direction in the subsoil layer that leads to more vertical stream tubes and a longer spatial correlation of particle velocities. In the layered K field, the dispersivity change with depth is almost identical to the one assumed by the STM model.

The simulated BTCs in the heterogeneous K-fields of the two decaying substances and the BTCs predicted by the three 1-D models are shown in Figure A16-15 (stationary K field) and Figure A16-16 (layered K field).
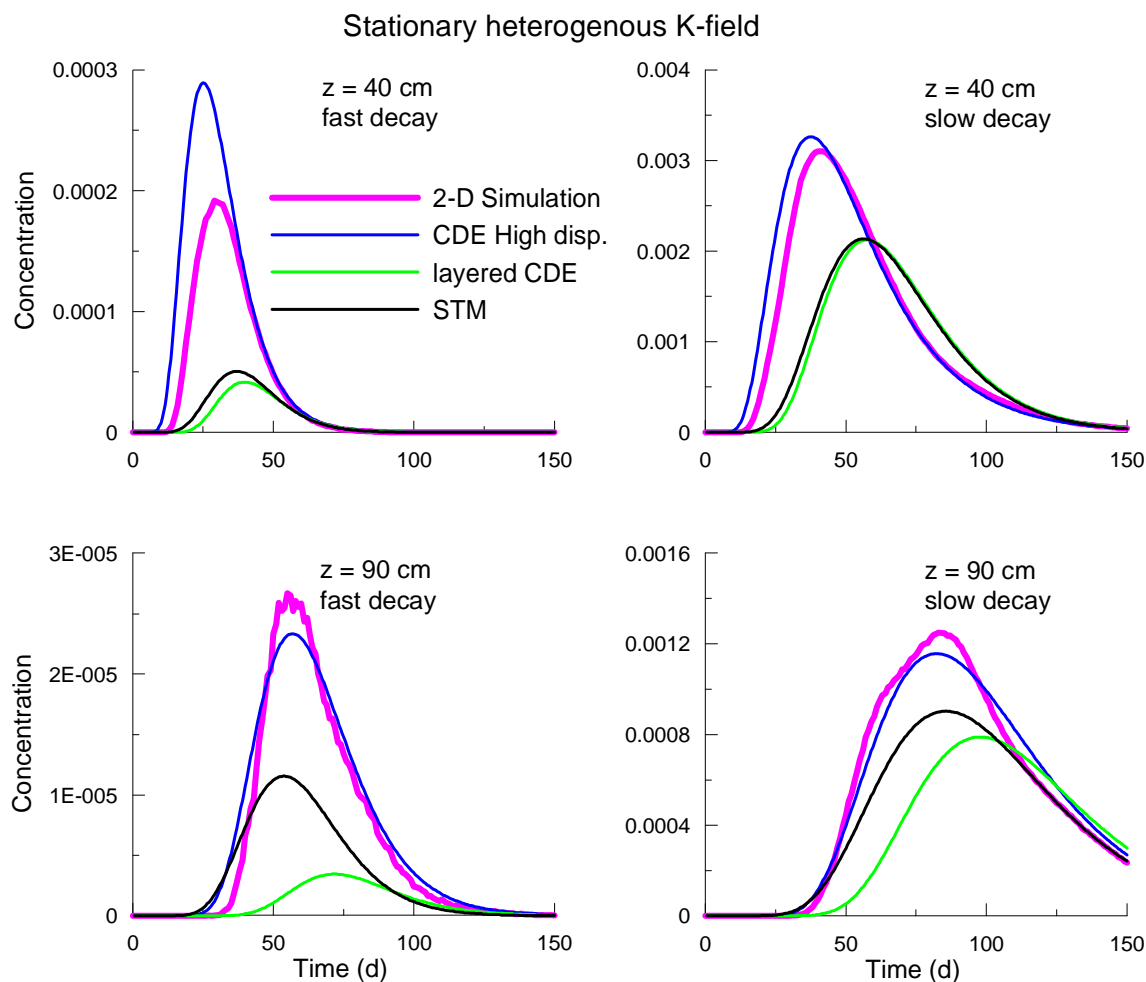
Figure A16-15. Simulated breakthrough curves of a fast (left panels) and slowly (right panels) decaying substance at 40 cm (top panels) and 90 cm (bottom panels) depth in a heterogeneous stationary K-field and predicted BTCs by three different 1-D models that predict the same breakthrough of an inert tracer at 90 cm depth.
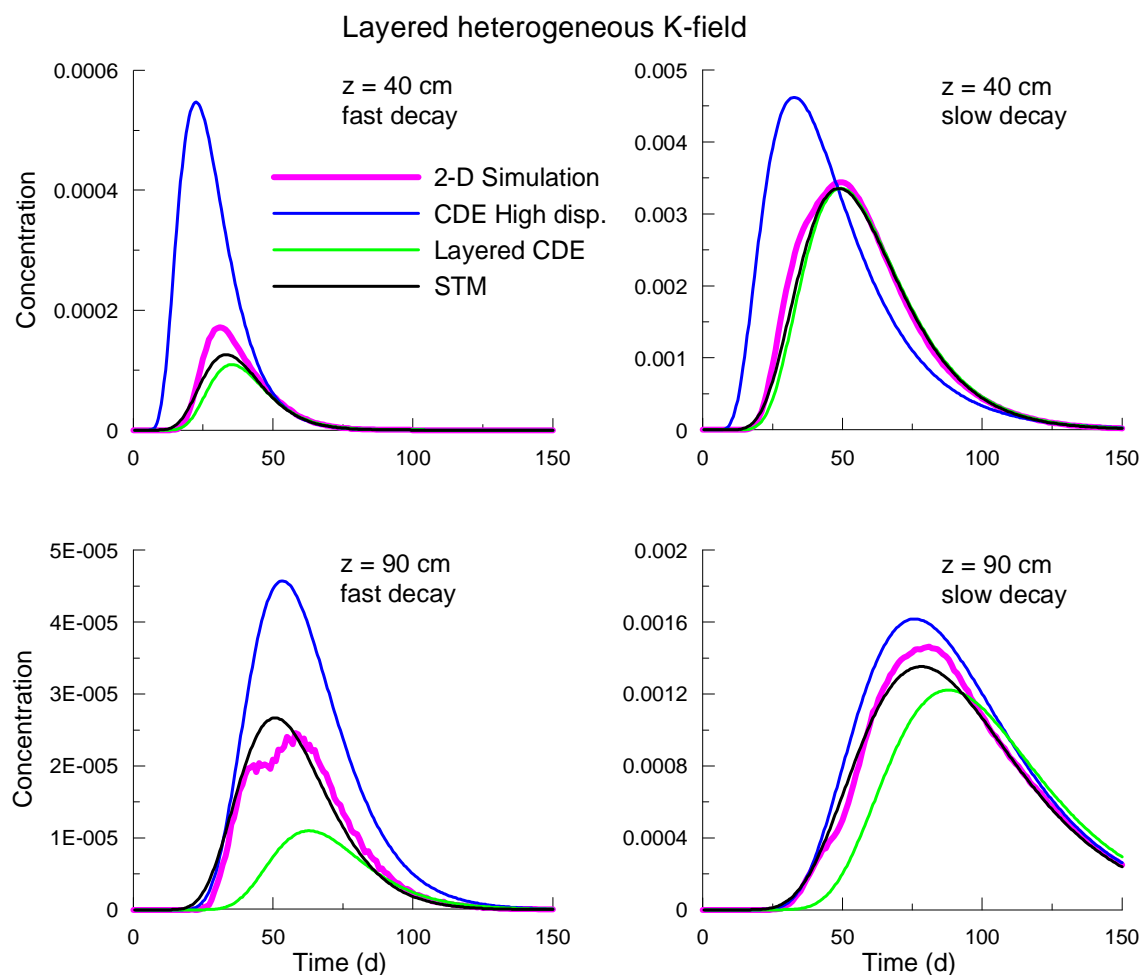
Figure A16-16. Same as Figure A16-15 but for a layered K-field.

In the stationary heterogeneous K-field, the CDE model with the high dispersivity best predicts the simulated BTCs of the fast and slowly decaying substances at 40 and 90 cm depth (Figure A16-15). The layered CDE and the STM underestimate the concentrations of the simulated BTCs, also at the bottom of the upper soil layer. This is explained by the underestimation of the dispersive solute flux through the upper soil layer, which is smaller in the layered CDE and STM than in the heterogeneous flow field (the dispersivity used for the upper soil layer in these models is smaller than the dispersivity in the heterogeneous flow field: see Figure A16-14). In the layered heterogeneous K-field, the dispersive flux through the first soil layer is similar in the layered CDE, the STM, and in the heterogeneous flow field. The simulated BTCs at 40 cm depth are therefore similar to the BTCs predicted by the layered CDE and the STM. The CDE with a high dispersivity, which assumes a larger dispersive flux through the upper soil layer, overestimates the simulated concentrations at 40 cm. As in Figure A16-9, the BTCs predicted at 90 cm depth by the STM and layered CDE

deviate despite similar predictions by both models at 40 cm depth. The simulated BTCs at 90 cm depth are best predicted by the STM whereas the layered CDE underestimates the simulated concentrations and leached mass fraction at 90 cm depth. This shows that in heterogeneous flow fields, particle velocities through different soil are correlated even when the hydraulic conductivity is not correlated across the layer boundaries. Therefore, the numerical simulations suggest that a layered CDE model that presumes uncorrelated particle velocities in different soil layers is not a realistic representation of transport in heterogeneous flow fields or soils in which the dispersivity length scales with travel distance. The CDE with a high dispersivity overestimates the simulated concentrations at 90 cm depth but to a lesser extend than the simulated concentrations at 40 cm depth.

Dispersivities of the layered CDE in the previous examples were calibrated so that the layered CDE and STM predict the same breakthrough of an inert tracer at the layer boundaries (i.e. at 30, 60 and 90 cm depth). An alternative way to calibrate the dispersivities of the layered CDE is to use the simulated inert tracer BTCs in heterogeneous flow fields (Figure A16-17).
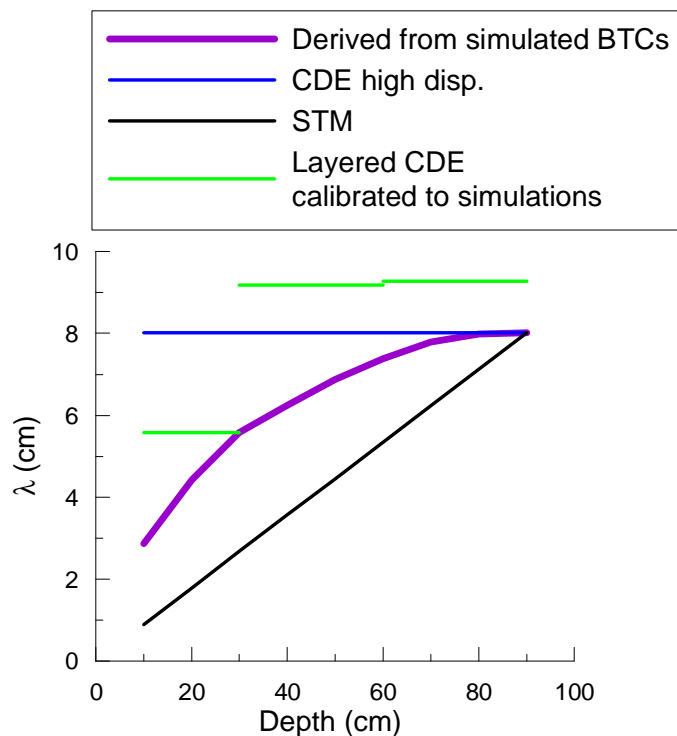
Figure A16-17. Dispersivity lengths (λ) derived from simulated flux weighted averaged inert tracer BTCs at different depths in the stationary heterogeneous K field. The dispersivities of the layered CDE model were defined so that the layered CDE predicts the same BTC as the simulated flux weighted averaged inert tracer BTCs in the heterogeneous flow field at 30, 60 and 90 cm depth. The STM and CDE model with constant dispersivity predict the same breakthrough BTC as the simulated flux weighted averaged inert tracer BTC in the heterogeneous flow field at 90 cm depth.

For the stationary heterogeneous K fields, the increase of dispersivity with increasing travel distance levels off with increasing travel distances, which points at an incomplete correlation of particle velocities along their trajectory. Because of the concave dispersivity versus travel distance curve, the STM underestimates the dispersion in the first soil layer. When the layered CDE is calibrated so that the dispersion in the first soil layer corresponds with that in the heterogeneous flow field, the layered CDE predicts a larger leached mass fraction of a reactive substance than the STM at 30 cm depth. In Figure A16-18, the breakthrough of fast decaying substance at 90 cm depth predicted by the layered CDE, the STM and the CDE with a constant dispersivity length are shown together with the simulated BTC in a stationary heterogeneous K-field.
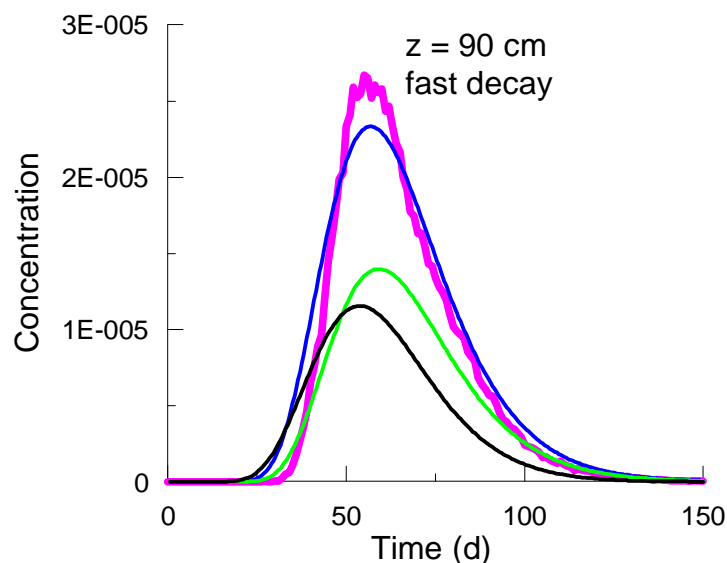
Figure A16-18. Simulated breakthrough curves of a fast decaying substance at 90 cm depth in a heterogeneous stationary K-field and predicted BTCs by three different 1-D models that predict the same breakthrough of an inert tracer at 90 cm depth (same legend as in Figure A16-15). The dispersivities of the layered CDE were calibrated from simulated BTCs in the heterogeneous K-field.

Also at 90 cm, the layered CDE predicts a larger leached mass fraction than the STM model. However, both the layered CDE and STM underestimate the simulated breakthrough in the heterogeneous flow field, which seems in this case best predicted by the CDE that assumes a constant dispersivity length.

This example illustrates that when particle velocities are imperfectly correlated along the particle trajectory, the STM may underestimate the leached mass fraction because it underestimates the dispersion in the first soil layer. Also a layered CDE, which is calibrated so that the dispersion in the first soil layer is correctly described, underestimates the leached mass fraction since the remaining correlation of particle velocities cannot be considered by the layered CDE model.

Conclusions

- A literature review of dispersivities indicates that the 5 cm dispersivity, which is currently used in the PEARL calculations, is more in agreement with the median of the distribution of experimentally determined dispersivities for a transport distance of 1 m than the 2.5 cm dispersivity, which is used in the PRZM and PELMO calculations.

- Dispersivities in finer textured soils were found to be larger than those in coarser textured soils but also for coarser textured soils, the 5 cm dispersivity corresponds better with the median value of the distribution than the 2.5 cm dispersivity.

- Dispersivity lengths were found to increase with travel distance indicating a general correlation of particle velocities along the trajectories of solute particles.

- In soil profiles with vertically varying decay and sorption constant, transport mechanisms within the soil profile must be correctly described in order to predict the leached mass fraction of a reactive substance. Different models which predict the same breakthrough of an inert tracer at the bottom of the soil profile but which use a different conceptualization of the transport within the profile lead to different predictions of leached mass fractions.

- To assess which model better represents the dispersion process in soils, numerical simulations of 2-D transport in heterogeneous hydraulic conductivity fields were carried out. Even in a layered heterogeneous conductivity field without a correlation of the hydraulic conductivity across soil layer boundaries, the layered CDE model, which presumes that particle velocities are not correlated across soil layer boundaries, underestimates the simulated breakthrough curves at the bottom of the soil profile. This study demonstrated that the STM, which assumes a correlation of particle velocities in different soil layers, better predicts transport, whereas the layered CDE underestimates and the uniform CDE overestimates the leached mass fraction. When the dispersivity versus travel distance curve is concave, which indicates an imperfect correlation of particle velocities, a layered CDE, which is calibrated so that the dispersion in the first layer is correctly predicted, may predict larger leached mass fractions than a STM, which underestimates the dispersion in the first soil layer, but still underestimates the leached mass fraction deeper in the soil profile because the correlation of particle velocities across layer boundaries cannot be accounted for by a layered CDE model. With decreasing particle velocity correlation (i.e. when the dispersivity versus travel distance curve becomes more concave), the simulated leached mass fractions in a heterogeneous flow field seems to converge more and more towards the predicted leached mass fraction by the homogeneous CDE model.

- Comparisons of the leached mass fractions predicted by a stream tube model (which is assumed to best represent the mechanism of transport in the soil) with those predicted by a convection dispersion model show that a convection dispersion model which assumes a hydrodynamically uniform soil profile and is parameterized with a dispersivity length that predicts the breakthrough of an inert tracer at the bottom of the soil profile provides a conservative estimation of the leached mass fraction. This conclusion can at present not

be extrapolated to substances with non linear sorption behaviour. For substances which do not sorb linearly, a stream tube model predicts an earlier breakthrough than a convection dispersion model. That means that a convective dispersion model cannot be considered as a conservative model for transport predictions of non-linearly sorbing substances. The degree of conservatism further depends on the vertical gradients of the decay and sorption constants, which are both assumed to decrease with increasing depth.

- The conservatism of the convection dispersion model, which is parameterized using the median value of the dispersivity distribution, must be put in context of the variation of the dispersivity distribution and the objective of a FOCUS scenario to represent a worst case condition. A further investigation of the conservatism of the convection dispersion model and its parameterization seems therefore desirable.

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depth cm	Disp cm	V cm/d	Vp cm/d	V_Vp	Jw cm/d	Jweff cm/d	experiment_number	Experimental_field	texture	Scale	concentration_type	measurement_technique	Type_of_flow	Source	year
105	10.85	8.14	8.19	0.99	2.85	2.85	1	Bekkevoort	l	column	flux	direct	steady	Vanderborght	2000
105	11.36	8.17	8.07	1.01	2.80	2.80	1	Bekkevoort	l	column	flux	direct	steady	Vanderborght	2000
105	17.99	19.37	19.02	1.02	6.80	6.80	2	Bekkevoort	l	column	flux	direct	steady	Vanderborght	2000
105	14.26	21.42	20.55	1.04	7.40	7.40	2	Bekkevoort	l	column	flux	direct	steady	Vanderborght	2000
105	3.66	3.79	3.82	0.99	1.30	1.30	3	Bekkevoort	l	column	flux	direct	steady	Vanderborght	2000
105	4.15	3.91	3.75	1.04	1.30	1.30	3	Bekkevoort	l	column	flux	direct	steady	Vanderborght	2000
70	3.77	7.37	8.00	0.92	2.84	2.84	4	Bekkevoort	l	field	resident	TDR	steady	Jacques	1998
90	6.23	7.13	8.00	0.89	2.84	2.84	4	Bekkevoort	l	field	resident	TDR	steady	Jacques	1998
105	26.80	6.70	8.20	0.82	2.80	17.60	5	Bekkevoort	l	column	flux	direct	intermittent	Vanderborght	2000
105	123.80	17.80	24.30	0.73	8.20	56.90	6	Bekkevoort	l	column	flux	direct	intermittent	Vanderborght	2000
55	19.96				0.28		7	Bekkevoort	l	field	resident	TDR	climatic	Jacques	2002
75	15.84				0.28		7	Bekkevoort	l	field	resident	TDR	climatic	Jacques	2002
95	21.72				0.28		7	Bekkevoort	l	field	resident	TDR	climatic	Jacques	2002
70	7.47	2.62	3.53	0.74	1.50	1.50	8	Krauthause	sil	field	resident	TDR	steady	Jacques	1998
90	6.59	2.62	3.52	0.74	1.50	1.50	8	Krauthause	sil	field	resident	TDR	steady	Jacques	1998
90	47.00		2.62		1.00	2.60	9	Bertem	sil	column	flux	calculated	intermittent	Vanderborght	1997
90	9.00		1.34		0.50	0.98	10	Bertem	sil	column	flux	calculated	intermittent	Vanderborght	1997
100	3.00	35.05	37.34	0.94	13.00	13.00	12	Geel	sl	column	flux	direct	steady	Vanderborght	2000
100	4.15	34.90	33.64	1.04	13.00	13.00	12	Geel	sl	column	flux	direct	steady	Vanderborght	2000
100	1.78	16.37	16.14	1.01	5.40	5.40	13	Geel	sl	column	flux	direct	steady	Vanderborght	2000
100	3.29	16.85	15.31	1.10	5.70	5.70	13	Geel	sl	column	flux	direct	steady	Vanderborght	2000
90	1.80	3.05	3.05	1.00	1.00	3.50	15	Geel	sl	column	flux	calculated	intermittent	Vanderborght	1997
100	1.40	7.26	7.55	0.96	2.50	5.80	18	Geel	sl	column	flux	direct	intermittent	Vanderborght	2000
100	4.30	6.45	6.61	0.98	2.30	10.30	18	Geel	sl	column	flux	direct	intermittent	Vanderborght	2000
100	4.40	4.52	4.43	1.02	1.00	1.00	19	Lommel	s	column	flux	direct	steady	Seuntjens	2001
90	39.00		2.98		1.00	2.50	20	Meer	ls	column	flux	calculated	steady	Vanderborght	2001
90	24.00		1.54		0.50	0.90	21	Meer	ls	column	flux	calculated	steady	Vanderborght	2001
150	1.87	8.40	7.78	1.08	1.40		22	Etiwanda	sl	field	resident	coring	interclim	Ellsworth	1991
169	10.83	7.54	7.78	0.97	1.40		22	Etiwanda	sl	field	resident	coring	interclim	Ellsworth	1991
198	9.05	8.40	7.78	1.08	1.40		22	Etiwanda	sl	field	resident	coring	interclim	Ellsworth	1991
60	13.70	1.77	3.24	0.55	0.55		23	Etiwanda	sl	field	flux	samplers	interclim	Butters	1989
90	23.90	1.90	3.67	0.52	0.55		23	Etiwanda	sl	field	flux	samplers	interclim	Butters	1989
120	15.70	2.12	3.93	0.54	0.55		23	Etiwanda	sl	field	flux	samplers	interclim	Butters	1989
180	20.20	2.29	3.67	0.63	0.55		23	Etiwanda	sl	field	flux	samplers	interclim	Butters	1989
60	25.71	2.80	4.00	0.70	0.60		24	Etiwanda	sl	field	flux	samplers	climatic	Jury	1985
90	15.14	3.70	4.00	0.93	0.60		24	Etiwanda	sl	field	flux	samplers	climatic	Jury	1985
120	19.83	3.60	4.00	0.90	0.60		24	Etiwanda	sl	field	flux	samplers	climatic	Jury	1985
180	15.74	4.30	4.00	1.08	0.60		24	Etiwanda	sl	field	flux	samplers	climatic	Jury	1985
61	25.14	0.83	0.58	1.42	0.18		25	Windsor	cl	field	resident	coring	interclim	Fleming	1995
80	7.49	1.02	0.58	1.75	0.18		25	Windsor	cl	field	resident	coring	interclim	Fleming	1995
80	14.54	0.75	0.58	1.28	0.18		25	Windsor	cl	field	flux	samplers	interclim	Fleming	1995
80	23.04	1.09	0.58	1.88	0.18		25	Windsor	cl	field	flux	samplers	interclim	Fleming	1995
120	9.78	0.68	0.58	1.16	0.18		25	Windsor	cl	field	flux	samplers	interclim	Fleming	1995
120	15.51	1.11	0.58	1.92	0.18		25	Windsor	cl	field	flux	samplers	interclim	Fleming	1995
158	5.44	0.69	0.58	1.18	0.18		25	Windsor	cl	field	resident	coring	interclim	Fleming	1995
160	9.70	0.73	0.58	1.26	0.18		25	Windsor	cl	field	flux	samplers	interclim	Fleming	1995
160	11.24	1.05	0.58	1.81	0.18		25	Windsor	cl	field	flux	samplers	interclim	Fleming	1995
62	1.50				0.40	0.40	27	Andelfinge	l	field	resident	dye	steady	Forrer	1999
100	9.05				0.92	0.92	32	Tinglev	s	column	flux	direct	steady	Jacobsen	1992
100	4.08				1.03	1.03	33	Tinglev	s	column	flux	direct	steady	Jacobsen	1992
100	1.89				1.18	1.18	34	Tinglev	s	column	flux	direct	steady	Jacobsen	1992
100	5.80				1.59	1.59	35	Tinglev	s	column	flux	direct	steady	Jacobsen	1992
100	3.86				1.63	1.63	36	Tinglev	s	column	flux	direct	steady	Jacobsen	1992

depth cm	Disp cm	V cm/d	Vp cm/d	V_Vp	Jw cm/d	Jweff cm/d	experiment_number	Experimental_field	texture	Scale	concentration_type	measurement_technique	Type_of_flow	Source	year
75	8.10	81.59	69.60	1.17	6.61	6.61	37	Basel	silg	column	flux	direct	steady	Buchter	1995
75	5.90	79.28	70.80	1.12	6.73	6.73	37	Basel	silg	column	flux	direct	steady	Buchter	1995
65	1.80	3.84	3.53	1.09	1.06	1.06	78	Riverside	sl	field	flux	samplers	steady	Ellsworth	1996
78	1.68	4.30	3.53	1.22	1.06	1.06	79	Riverside	sl	field	resident	coring	steady	Ellsworth	1996
115	2.46	4.42	3.53	1.25	1.06	1.06	79	Riverside	sl	field	resident	coring	steady	Ellsworth	1996
60	13.47	14.60	13.52	1.08	4.84	4.84	85	Phoenix	cl	field	resident	samplers	steady	Jaynes	1993
100	13.50	17.37	13.57	1.28	4.84	4.84	85	Phoenix	cl	field	resident	samplers	steady	Jaynes	1993
140	6.73	13.48	13.61	0.99	4.84	4.84	85	Phoenix	cl	field	resident	samplers	steady	Jaynes	1993
180	7.49	16.24	13.77	1.18	4.84	4.84	85	Phoenix	cl	field	resident	samplers	steady	Jaynes	1993
80	5.31	8.56	7.40	1.16	1.25	1.25	91	Delhi(ON)	ls	field	flux	samplers	steady	Ward	1995
85	8.22	25.74	25.00	1.03	4.00	4.00	92	Delhi(ON)	ls	field	resident	coring	steady	Ward	1995
66	2.41	1.94			0.26		96	Nienwohlde	ls	field	resident	coring	climatic	Salzmann	1995
70	28.30	0.40			0.14		97	Fuhrberger	s	field	flux	samplers	climatic	Deurer	2001
110	12.10	1.15			0.14		97	Fuhrberger	s	field	flux	samplers	climatic	Deurer	2001
84	29.00	0.38			0.56	14.40	175	Bulach	l	field	flux	samplers	interclim	Roth	1991
70	6.20	0.73			0.23		186	Hupsel	ls	field	resident	coring	climatic	van Ommen	1989
70	19.80	0.69			0.23		186	Hupsel	ls	field	resident	coring	climatic	van Ommen	1989
100	12.29	5.38	4.27	1.26	0.99	0.99	188	Lommel	s	column	flux	direct	steady	Seuntjens	2001
70	6.52	25.64	18.25	1.40	4.00		189	Loddekopin	ls	field	resident	TDR	intermittent	Persson	2002
90	5.28	27.18	19.90	1.37	4.00		189	Loddekopin	ls	field	resident	TDR	intermittent	Persson	2002
70	19.99	15.37	8.53	1.80	1.87		190	Loddekopin	ls	field	resident	TDR	intermittent	Persson	2002
90	6.66	16.52	9.31	1.78	1.87		190	Loddekopin	ls	field	resident	TDR	intermittent	Persson	2002
150	40.94	3.90	4.66	0.84	2.00	2.00	193	New Mexico	sic	field	resident	samplers	steady	van de Pol	1977
80	3.45	1.12	1.12	1.00	0.36		194	Beotia	cl	column	flux	direct	intermittent	Cassel	1974
80	4.51	1.05	1.05	1.00	0.36		195	Aberdeen	cl	column	flux	direct	intermittent	Cassel	1974
120	9.20	0.29	0.29	1.02	0.11		200	Merzenhaus	sil	column	flux	direct	climatic	Kasteel	2004
120	5.70	0.23	0.29	0.80	0.11		201	Merzenhaus	sil	field	flux	samplers	climatic	Kasteel	2004
122	2.90	0.74			0.12		205	Blumberg	sl	field	resident	coring	climatic	Hammel	1999

APPENDIX 17. DISPERSIVITY IN THE FOCUS MODELS

P.J.J Sweeney and J.S Dyson

Background

The theory of dispersion of solutes in narrow tubes was first developed by Taylor (1953). This theory was first applied to the consideration of the transport of solutes within aquifers, for which the following characteristics were found (Gelhar et al., 1992, Dagan 1986, Pickens et al., 1981): dispersion initially rises rapidly and is scale-dependent up to a certain length and then is constant. Aquifers present an ideal system in which to study solute dispersion because the longitudinal movement of a solute can be tracked over large distances (up to 10^4m in Gelhar et al 1992), statistical homogeneity of a single stratum or multiple relatively confined strata that are parallel to the direction of flow is usually a valid assumption (Matheron and De Marsily, 1980), and, because the porous medium is saturated, the variation in saturated hydraulic conductivity only needs to be considered.

Dispersion of a solute moving downwards through a layered, unsaturated soil is much more complex. Soils are highly heterogeneous in the direction of solute transport, and an assumption of statistical homogeneity of soil properties (i.e. where soil properties do not vary on average with distance) difficult to justify. Movement of the solute can be multi-directional due to the transient hydrological and upper boundary conditions, primarily downward transport is perpendicular to the layering of the medium, and unsaturated hydraulic conductivity is a non-linear function of the volumetric water content. Nevertheless, two main approaches to solute transport within unsaturated soils have emerged. These are the Convective Dispersive Equation (CDE) and the convective lognormal transfer model (or Stream Tube Model STM) of Jury (1982).

The CDE equation considers that when a solute travels across a boundary the solute contains no "memory" of transport in the previous layer. The STM assumes transport of solute in soils to be confined to a number of different tubes of different diameters and hence different transport velocities. This means, in contrast to the CDE, that solute confined to a fast-moving tube will remain in that tube when crossing a layered boundary, and there is no interchange with solute in a slow moving tube. The STM therefore assumes perfect correlation across different soil layers whereas the CDE assumes zero correlation. These two models can be considered to be opposing idealisations of solute transport in soils.

An important corollary of these models is that in the CDE dispersion is constant with distance whereas it scales with length in the STM. Modelling of solute transport in soils has predominantly used the CDE because the equations of solute transport are easy to solve numerically, and allow for upward transport of water within the soil profile for example by evapotranspiration by plants. In contrast the STM has not been used to the same extent in models because numerical solution is more complex, and how this model would accommodate upward movement of water as a result of evapotranspiration is unclear. Similarly, picturing how perfectly idealised stream tubes are realised in agricultural fields experiencing regular tillage operations is difficult and validating the integrity of the "stream tubes" during transient soil hydrological conditions by experiment is almost impossible.

As noted by Flury et al. (1998) the experimental investigation of the mechanisms of solute transport in soils are far from conclusive. Butters and Jury (1989) found an apparent increase in dispersivity with distance for a bromide tracer over the first 3m of soil, but then found an apparent decrease in dispersivity from 3m – 4.5m which they attributed to a different soil layer at 3m. Conversely Ellsworth and Jury (1991) found that the CDE was a better representation of dispersion at the same site. Roth et al (1991) found that the STM gave a poor fit to data in a layered soil. Zhang (2000) found that the CDE represented the breakthrough in soil columns up to 30cm reasonably well, but was a poor fit to data for deeper depths, where the STM model was a better fit, Nissen et al. (2000) had similar findings. However Zhang (2000) also found that the STM was not a good fit to data collected from highly heterogeneous soil columns. Si (2002) found that flow pathways within a field soil were dependent upon application rate and concluded that the STM model was not applicable to this soil. Shukla et al (2002, 2003) observed that the CDE represented the breakthrough of an inert solute in soil columns containing a number of different soils and under a number of different flow velocities. Javaux and Vanclooster (2003) in experiments with a sandy monolith found that the CDE equation was appropriate for depths up to 30cm but that the STM represented solute leaching better for depths > 1m. Vanderborght et al (2002) similarly found the CDE to be appropriate for breakthrough of a fluorescent tracer up to a depth of approximately 30cm but that dispersion followed a STM type process deeper than this. Heuvelman and McInnes, (1998) observed that both the CDE and STM fitted the breakthrough of an inert tracer in a layered soil up to 30cm, but also found that dispersion at this depth was a poor predictor of leaching at 90cm and 120cm.

Experiments on the breakthrough of inert tracers therefore present no clear pattern with regard to the CDE and STM models. In some cases the CDE model is an appropriate model of solute breakthrough in others it is the STM and in yet other cases neither is appropriate.

These findings emphasise the complexities involved in determining the dispersion of a substance in a highly heterogeneous medium such as soil. Flury et al (1998), in a review, suggested that the CDE might be the more appropriate model to use where there is pronounced layering in soil and that the STM model may be more appropriate for more homogeneous soils, and therefore that the dispersion was likely to be site specific. Jury and Scotter (1994) also concluded that the STM was less likely to be applicable where there was distinct layering in soils, because layering would be expected to enhance lateral mixing that is characteristic of CDE type behaviour.

Experiments designed to measure dispersion length show a wide scatter. For example data collected by Flury et al. (1998) showed that dispersion length measured at 1 m varied between about 1 and 100cm. Figure A17-1 shows the values of dispersion length collected from the literature by this FOCUS group for 30cm, 60cm and 100cm depths. These data, which were selected to be relevant to agricultural conditions, show a variation of at least an order of magnitude for dispersion length.
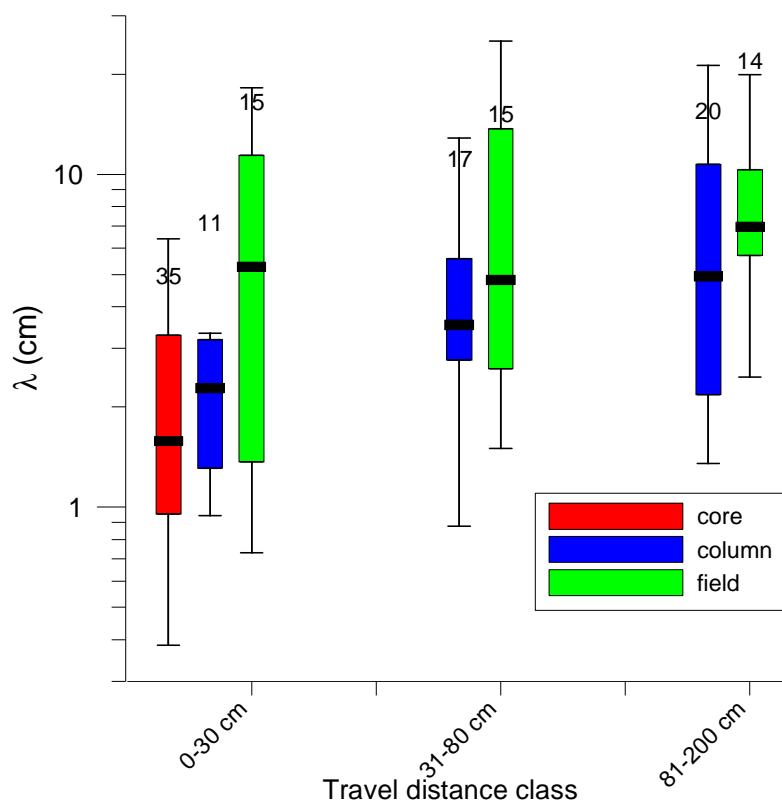
Figure A17-1. Data collected on dispersion length measurements by FOCUS GW II

Dispersion Length in FOCUS Leaching Models

Table A17-1 shows the characteristics of the soils used in the FOCUS Châteaudun and Hamburg scenarios.   This table shows that these soils are layered both in the sense that hydraulic properties vary with depth (they are therefore not statistically homogeneous), and that solute reaction parameters such as sorption and degradation properties vary. There is also variation between scenarios. The depth dependent variation in degradation and organic carbon content mean that the top 30 cm of soil is critical, because this is where most degradation and adsorption will occur. The layering of hydraulic properties implies that some degree of lateral mixing might be expected in field soils having these properties.

Table A17-1. Characteristics of soils in the FOCUS Châteaudun and Hamburg scenarios.

Location	Depth (cm)	%OC	Water content 10Kpa	Water Content 1600kPa	K_{sat} (Units of 10^{-6} ms^{-1})	Depth Factor
Châteaudun						
	0 -25	1.39	0.374	0.253	20	1
	25 – 50	0.93	0.372	0.235	30	0.5
	50 – 60	0.7	0.372	0.235	50	0.5
	60 – 100	0.3	0.386	0.185	12	0.3
Hamburg						
	0 – 30	1.5	0.292	0.064	23.3	1
	30 – 60	1	0.277	0.047	31.7	0.5
	60 – 75	0.2	0.229	0.040	28.3	0.3
	75 – 90	0	0.163	0.022	28.3	0.3
	90 – 100	0	0.163	0.022	28.3	0.3

FOCUS leaching models consider that dispersion of a solute occurs according to the CDE. The PEARL model uses a constant dispersion length of 5 cm whereas the PELMO/PRZM models assume a constant dispersion length of 2.5 cm. Comparison with Figure A17-1 shows that the dispersion length used by the PELMO/PRZM models is more representative of the breakthrough of an inert tracer at 30 cm (i.e. through the most reactive soil layer) and that the dispersion length used by the PEARL model is more representative of the breakthrough of an inert tracer at 1 m depth (i.e. the depth for evaluation).

The problem with harmonising dispersion length in the FOCUS models arises because the experimental data on dispersion length are very variable and because the experimental measurement of dispersion is likely to vary between locations as a result of variations in hydraulic properties, which means that it may be difficult to distinguish between a dispersion length of 2.5 cm and 5 cm with a high degree of accuracy. Note that the majority of data on dispersion are for non-reactive solutes, and data on dispersion of reactive solutes moving through layered systems where there are differing rates of adsorption and degradation are sparse. Clearly, if one soil layer is much more reactive than others then the dispersion in this layer is critical, because it will control the mass of solute entering into other layers. However the dispersion in deeper soil layers is also important as it will influence the mass leaching to 1 m. It should also be borne in mind that the leached mass fractions that result in a leachate concentration of 0.1 µg/L in soil pore water are extremely small (approximately 0.1% of a 1 kg/ha application) which demands a high degree of precision from model predictions, one which is difficult to extract from the available data on dispersion length.

Different assumptions on the mechanism of solute spreading, i.e. the STM or CDE in layered soils, give different leached mass fractions at 1m for reactive solutes. The STM parameterised to give a dispersion length of 6 cm at 1m gave a much greater leached mass fraction at 1 m depth than the CDE with a constant dispersion length of 1.8 cm (value of dispersion according to the STM at 30 cm) but the agreement was closer with a constant dispersion length of 5 cm – although it should be noted that the leached mass fractions for the 5 cm dispersion length exceeded the STM model predictions in all cases.

The difficulty with the application of the STM is that, as noted above, there is no conclusive evidence from the literature that it applies in all situations and, as noted by Jury and Scotter (1994), it is less likely to be valid in situations where there is layering of the soil. It can therefore be regarded as an extreme model of solute transport which requires perfect correlation and soils to be statistically homogeneous (i.e. mean properties do not change with distance). Note also that the STM calculation assumes that water movement is always downwards and it is not known how upward movement of water resulting from evapotranspiration by plants can affect dispersion.

The soils in the FOCUS scenarios are layered in terms of their reactivity and their hydraulic properties (i.e. they are not statistically homogeneous), some lateral mixing can therefore be expected. Therefore, predictions using the STM represent an upper bound. This would imply that the CDE using a 5 cm dispersion length gives leached mass fractions that are too

high, conversely the CDE using a dispersion length of 1.8 cm is too low, because the dispersion at 30 cm is used to estimate dispersion through the whole soil profile.

Hydrological modelling using K-fields has not been used to evaluate the FOCUS models before. The key factor with regard to these models lies with the correlation length in the vertical and horizontal directions chosen for the various soil properties.   Figure A17-1 shows K-field modelling performed for a field site by Rockhold and Rossi (1996). This Figure shows that using a correlation length of 440 cm in the horizontal direction and 45 cm in the vertical direction, resulted in horizontal flow field features, which would be more likely to show lateral mixing and hence CDE type behaviour. Similarly, Russo and Bouton (1992) used a horizontal correlation length of 83cm for Log Ksat in the horizontal direction and 19cm in the vertical direction, which again resulted in more layered than stream tube like structures. Also, Roth and Hammel (1996) have shown that the transition between short term stream tube behaviour and long-term CDE type behaviour is dependent upon the assumptions made regarding underlying soil heterogeneity. In summary therefore there are no generally accepted values in the literature for the vertical and horizontal correlations for critical soil parameters and the choice of these parameters has a critical impact on whether structures are layered or "tube like". Therefore likely either "stream tube like" or "layered type" behaviour can be shown by suitable choice of parameters and which values are generally appropriate is not clear. Similarly how the upward movement of water as a result of evapotranspiration would affect the results of the modelling is unclear.
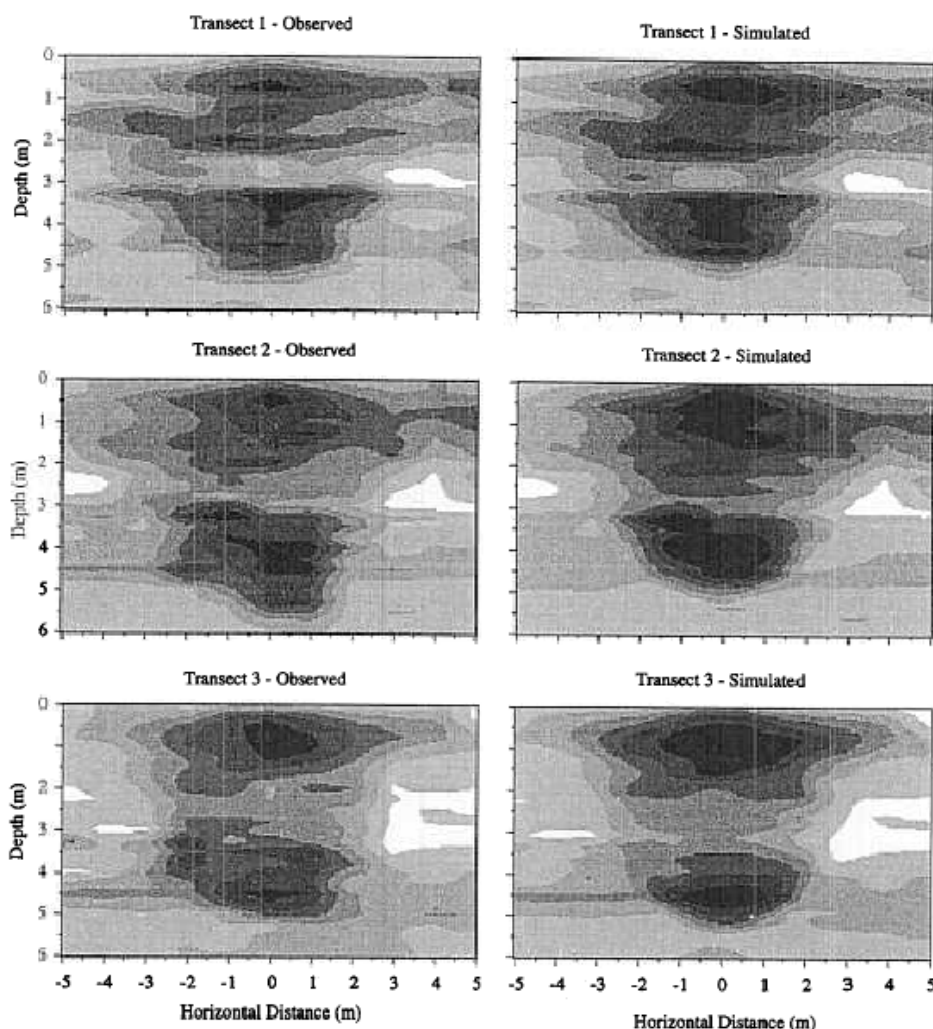
Figure A17-1. K-field modelling performed by Rockhold and Rossi (1996).

Proposal for Dispersion Length In FOCUS Leaching Models

The general features of dispersion in soil may be summarised as follows:

- Dispersion length would be expected to increase with depth up to a certain limit.
- The STM and CDE are different idealisations of solute transport in soils and will be applicable in some instances and not in others.
- Experiments on dispersion show a high degree of variability in the dispersion length both within site and between sites.
- Experimental data on dispersion length of reactive solutes are sparse.

In order to provide a realistic estimate of dispersion length that will give a reasonable estimate of dispersion length for all of the soil profiles in the FOCUS ground water scenarios, the use of the collection of experimental determinations of dispersion length seems appropriate. These data represent the best available data on dispersion length relevant to

agricultural soils and the values derived from them should be a reasonable estimate of dispersion length in the FOCUS scenarios in the absence of site-specific values.

The most critical layer for adsorption and degradation is the topmost layer (approximately 30 cm) in the FOCUS scenarios, corresponding to the plough layer.

The median dispersivity for the soils in the dispersivity data base for depths between 25 – 35 cm is 2.8 cm – excluding ponding and interponding data, and flow rates >10cm/day. This value is very close to that used by the PELMO and PRZM models, however an appropriate value for dispersion in this layer could conservatively be chosen to be 3 cm. A value of 5 cm for this layer is however inappropriate because it suggests a value much higher than measurements and also theoretical calculations show that leached mass fractions using this assumption exceed those of the STM model in all cases.

At 1 m depth the experimental data suggest that a dispersion length of 6 cm is appropriate, which indicates that using a constant dispersion length of 1.8 cm and 2.5 cm for the whole profile is inappropriate. Dispersion in intermediate layers could be obtained be linear interpolation between the 3 cm value at 30 cm depth and the 6 cm value at 1 m depth. The revised parameterisation of the layered CDE model is shown in Table A17-3.

Table A17-3. Different idealisations of the dispersion length data.

Layer(cm)	λ (z) STM	λ (i) Layered CDE	λ Constant CDE (cm)
0 – 30	1.8	3	6
30 – 60	3.6	5.6	6
60 – 100	6	8.6	6
Profile Average	6	6	6

Although each of the idealisations in Table A17-3 will give the same breakthrough of an inert tracer at 1 m, there are important differences between them. In the STM model the dispersion length for *any* 30 cm block of material will be 1.8 cm i.e. if the 30 – 60 cm layer was isolated from the rest of the profile and a dispersion experiment were performed upon it, the dispersion length would be 1.8cm. This results from the requirement of statistical homogeneity of soil properties for the STM. The STM therefore pictures the soil to be the

same throughout the top 1m. In contrast the layered CDE assumes that the different layers of material behave differently, i.e. if a dispersion experiment was performed on the 30 – 60 cm block of material it would result in a value of dispersion on 5.6cm. For the constant CDE model a dispersion experiment performed on any portion of any layer, or combination of layers will yield a dispersion length of 6cm.

In reality, transport of solutes in soil is likely to be somewhere in-between the CDE and STM. On the one hand, regions of fast flow are likely to be correlated to some extent across a layered boundary, on the other some lateral mixing at a layered boundary is likely as well so that the assumption of perfect correlation across a boundary is a theoretical extreme. The layered CDE represents a compromise between the two models of solute dispersion. Dispersion length increases with depth in the soil profile, and the parameterisation in Table A17-3 will give the same breakthrough of an inert tracer at 1m as the STM. Unlike the STM however, each soil layer behaves differently, as if it were different material. This is consistent with the picture of soil having different structure in the plough layer through regular tillage operations and then graduating to a more blocky structure with depth. The layered CDE is similar to the constant CDE because each of the layers has a constant dispersivity.

In order to test this parameterisation of the layered CDE model, simulations were carried out with the models in Table A17-3 for reactive solutes having a number of different substance properties likely to result in leachate concentrations close to 0.1 µg/L. For these simulations a soil having a bulk density of 1.4 g/mL and a volumetric water content of 0.3 was assumed, as was a constant percolation rate resulting in a cumulative percolation of 300 mm/year. Standard FOCUS assumptions for solute reactivity in the 0 – 30, 30 – 60 and 60 – 100 mm layers was also assumed. The results of this modelling are shown in Table A17-4, concentration profiles predicted by the various models for a substance having a K_{oc} of 30 and a half-life of 40 days are shown in Figure A17-2.

Table A17-4. Leached mass fractions for the different idealisations of the dispersivity data.

Half-Life(d)	K_{oc}	Stream Tube mass fraction leached	CDE 6 cm mass fraction leached	Layered CDE Mass fraction leached
50	10	0.020	0.022	0.017
20	10	3.05E-04	3.96E-04	1.88E-04
40	30	5.47E-04	7.98E-03	3.76E-04
80	60	1.43E-04	2.10E-03	1.10E-03
120	90	2.00E-03	2.95E-03	1.59E-03
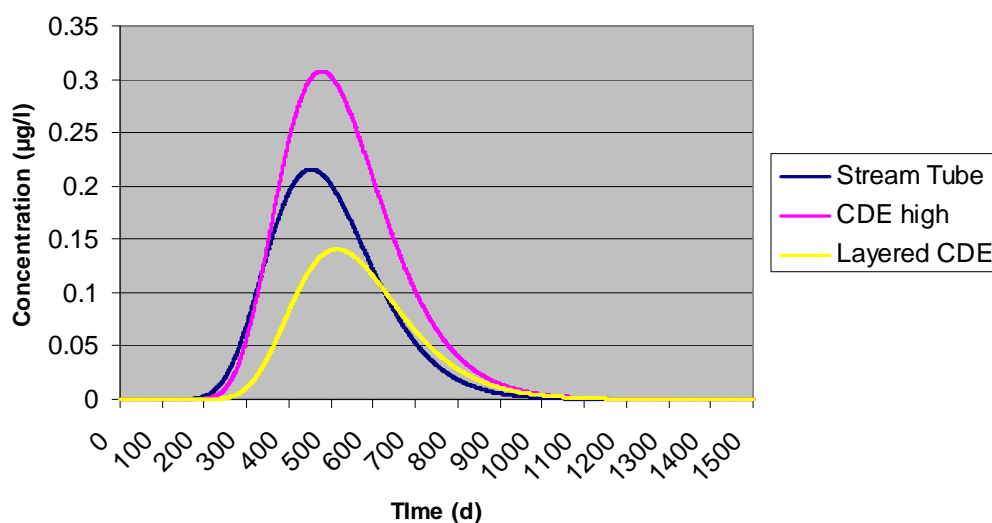
Figure A17-2. Breakthrough curves predicted by the various models for a solute having a K_{oc} of 30 and a half-life of 40 days

Figure A9-2 and Table A9-4 show that the predictions of the stream tube model lie in-between those of the CDE high (CDE with dispersion = 6 cm) model and the layered CDE model in every case. However the data suggest that the constant CDE model exceeds the leached mass fraction compared to the stream tube model by approximately the same amount as the layered CDE is less than the stream tube model i.e. determining from these data which of these models is the "better" fit to the stream tube model is very difficult. However, since the stream tube model is an extreme idealisation of solute transport in soils, the fact that the CDE predicts greater leaching in every instance in Table A17-4, suggests that this model is over predicting the leachate of a reactive solute in a layered system. Note

that in terms of the FOCUS models the most relevant quantity to consider is the leached mass fraction i.e. the area under each curve in Figure A9-1, because this quantity is more similar to the output in assessments.

A key consideration in the construction of the layered CDE model was of zero correlation of particle velocities across a layered boundary. A method by which transport across boundaries may be correlated using the CDE model is provided at the end of this appendix. Although this results in slightly changed values for dispersion in the various layers, the general results outlined above are effectively unchanged.

Conclusions

- The available data on dispersion of solutes in soil are far from clear; the data show a wide degree of scatter and are based upon dispersion of inert tracers rather than reactive substances. In addition there is no conclusive evidence from the literature that solute transport should be stream tube or CDE and likely transport is site specific and each model will apply in some circumstances and not in others.

- How appropriate vertical and horizontal correlation distances should be chosen for soil transport properties in K-field modelling is not clear from the literature. These correlation lengths have a critical impact upon whether transport is likely to be stream-tube like or like the CDE. Also how upward movement of water as a result of evapotranspiration and the use of unsaturated water contents would affect results of this modelling is not clear. Therefore whether highly complex K-field modelling can be regarded as definitive is open to question.

- The data on dispersion collected by this FOCUS group show that in general dispersion increases with depth, that a value for dispersion of 3 cm is appropriate for the top 30 cm of soil (which is the most reactive), and that a value of 6 cm is appropriate for dispersion at 1 m. Any parameterisation of FOCUS models, which are based upon the convection dispersion equation, to these data will require some form of approximation and whatever approximation is used will affect concentrations at 1m in a layered system. Given the requirement for models to predict concentrations of substances to a precision of approximately 0.1% of an application, and the high degree of variability of the dispersion measurements, again whether it is possible to accurately distinguish between a dispersion of 2.5 cm and 5 cm with a high degree of statistical certainty is open to question. Nevertheless, parameterising models to

represent the general features found in experiment while concentrating on the most reactive layer i.e. 30 cm seems appropriate.

- The layered CDE is an appropriate choice for dispersion in the FOCUS models because:
  - o It uses a value of dispersion (3 cm) more appropriate to dispersion in the critical, most reactive topmost layer of soil and one which is in better agreement with the values in the dispersivity data base than the 6 cm value.
  - o Gives predictions for the breakthrough of an inert tracer at 1 m that are consistent with the data from the dispersivity data base.
  - o Gives predictions for leached mass fractions of reactive solutes that are in as good agreement with the values of the stream tube model as the constant CDE model. However, since the stream tube model is an extreme of solute transport requiring perfect correlation between layers and transport parameters that do not change, on average, with depth, the fact that constant CDE model exceeds the leached mass fractions predicted by the stream tube model for a reactive solute indicate that it predicts a leached mass fraction that are too high for reactive solutes.
  - o Is a suitable compromise that fits the observed features of the measured data on dispersion (i.e. increases with depth) and is consistent with the generalised picture of agricultural soils being well-tilled and homogeneous in the plough layer and more blocky and structured with depth.

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Inclusion of Correlation in the Layered CDE Model

A layered CDE model has been developed that implicitly incorporates some growth in dispersivity with distance by lumping it into the dispersivity for each layer initially, this was done in a simple way using a mean dispersivity of 3cm at 30cm depth and 6cm at 100cm depth. To do this a linear interpolation was made to 60cm, giving a total dispersivity to 60cm of 4.29cm. If it is assumed that flow velocities are the same in each layer, and that there is zero correlation between each layer then the relation between the dispersivity to a given depth and that or the individual depth increments is given by the following for three layers.

$$Z_T\lambda_T = Z_1\lambda1 + Z_2\lambda_2 + Z_3\lambda_3 \qquad\qquad (A17\text{-}1)$$

Where

$Z_T = Z_1 + Z_2 + Z_3$ (the total depth)

λ_T is the overall dispersivity

$\lambda_{1,2,3}$ = is the dispersivity of layers 1,2,3

Re-arrangement of Equation A17-1 with two layers leads to:

$$\lambda_2 = \frac{Z_T\lambda_T - Z_1\lambda_1}{Z_2} = \frac{(60 \times 4.29) - (30 \times 3)}{30} = 5.58 \qquad\qquad (A17\text{-}2)$$

and arrangement into Equation A17-1 with three layers leads to:

$$\lambda_2 = \frac{Z_T\lambda_T - Z_1\lambda_1 - Z_2\lambda_2}{Z_3} = \frac{(100 \times 6) - (30 \times 3) - (30 \times 5.58)}{40} = 8.565 \qquad (A17\text{-}3)$$

However, since dispersivity is growing between 30 cm and 100 cm assuming that there is some correlation between each layer may be more realistic, since Equation A17-1 tends to make the dispersivities in each layer successively larger and potentially unrealistic. In order to try taking correlation into account, several steps and some further assumptions need to be made.

First, Equation A17-1 needs to be expanded to account for the cross-correlation between the travel times in each layer. This results in

$$Z_T\lambda_T = Z_1\lambda_1 + Z_2\lambda_2 + Z_3\lambda_3 + 2\rho\sqrt{(Z_1\lambda_1\ Z_2\lambda_2)} + 2\rho\sqrt{(Z_1\lambda_1\ Z_3\lambda_3)} + 2\rho\sqrt{(Z_2\lambda_2\ Z3\lambda_3)} \quad (A17\text{-}4)$$

Where ρ is the correlation coefficient between the layers. If correlation is less than perfect i.e. <1 then the value of this should vary or decline with depth, as predicted by dispersion theory.

Secondly, in order to solve Equation A17-4, an assumption needs to be made about the functional form of ρ over depth, which must be a declining function with depth. The simplest approach is to take the bonded linear model (c.f. Webster and Oliver, p228, 1990) in which

$$\rho = 1 - \alpha \Delta Z \qquad \text{(A17-5)}$$

where α is the constant describing how rapidly $\rho \rightarrow 0$ over depth and therefore must be in the range α > 0, and ΔZ is the distance between the upper layer and the bottom of the lower layer.

Thirdly, also to solve Equation A17-4, an assumption needs to be made about the dispersivity in each layer, namely that the dispersivity of each layer is the same at a depth of 30 cm i.e. 3 cm. However, given that the third layer is 40 cm, Equation 9A-4 cannot be solved since this is not known. Nevertheless, if the dispersive properties of each layer follow the same process, then it could be assumed that 3 cm < λ < 4 cm. If the third layer is split into two sublayers, layer 3a of 30 cm and layer 3b of 10 cm with dispersivities of 3 cm and 1 cm respectively. This allows Equation A17-4 to be expanded and after substitution of Equation A17-5 into Equation A17-4, the value of α can be solved that satisfies the overall growth in dispersivity from 3 cm at 30 cm to 6 cm at 100cm.

$$\alpha = \frac{Z_1\lambda_1 + Z_2\lambda_2 + Z_3\lambda_3 - Z_T\lambda_T + A_{sum}}{[(A_{1,2}\Delta Z_{1,2}) + (A_{1,3a}\Delta Z_{1,3a}) + (A_{1,3b}\Delta Z_{1,3b}) + (A_{2,3a}\Delta Z_{2,3a}) + (A_{2,3b}\Delta Z_{2,3b}) + (A_{2,3b}\Delta Z_{2,3b})]} \qquad \text{(A17-6)}$$

Where $A_{1,2} = 2\rho\sqrt{(Z_1\lambda_1 Z_2\lambda_2)}$ etc. and A_{sum} is the sum of all of them,

and $\Delta Z_{1,2} = T Z_2 - T Z_1$
Where T Z1 is the total depth of the soil to the bottom of layer 1 etc.

Equation A17-4 can now be used to calculate how much dispersivity has grown overall by the depth of 60 cm, after substitution of Equation A17-5 into A17-4.

$$\lambda_T = \frac{[Z_1\lambda_1 + Z_2\lambda_2 + 2(1 - \alpha\Delta Z_{1,2}) \sqrt{(Z_1\lambda_1 Z_2\lambda_2)}]}{Z_T} \qquad \text{(A17-7)}$$

The results give a value for α of 0.0139 and the value of λ_T of 4.75 cm at 60 cm (somewhat higher than the value of 4.29 given by linear interpolation).

Finally to determine the dispersivity values for each layer if the layered CDE is used to implicitly incorporate the growth of the dispersivity, then Equations A17-2 and A17-3 can be used to lump this growth giving:

$$\lambda_2 = \frac{(60 \times 4.75) - (30 \times 3)}{30} = 6.5\text{cm}$$

$$\lambda_3 = \frac{(100 \times 6) - (30 \times 3) - (30 \times 6.5)}{40} = 7.9\text{cm}$$

APPENDIX 18. COMPARISON OF MARS AND FAO POTENTIAL REFERENCE EVAPOTRANSPIRATION

The reference evapotranspiration data used in the FOCUS ground water scenarios were inferred from the MARS data base. The potential crop evapotranspiration data were obtained by multiplying these reference evaporation data (abbreviated as ET0_MARS) with crop coefficients (kc coefficients). However, the crop coefficients used in the FOCUS ground water scenarios were based on the data reported by the FAO, in particular the FAO crop water requirement calculation procedures (e.g. Allen et al., 1998). The FAO kc procedure, however, is based on the ET0 procedures proposed by FAO, which will be referred to as ET0_FAO. In principle the kc factors may only be combined with ET_FAO since kc factors have been obtained by dividing the measurement of the potential evapotranspiration in field and lysimeter studies with ET0_FAO. Although both ET0_MARS and ET0_FAO are based on the Penman Monteith equation, the ET0_FAO and ET_MARS will not necessarily be the same since different parameterisation schemes are used for the surface and aerodynamic resistance terms in the Penman Monteith equation. Therefore inconsistencies may appear when combining FAO based kc factors with ET0_MARS.

Procedure for calculating ET0_FAO from the MARS data base

All calculations were based on the FAO recommendations as described by Allen et al., (1998). The basic formula was (Allen et al., 1998, Equation 6):

$$ET_o = \frac{0.408\Delta(R_n - G) + \gamma \dfrac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)} \qquad \text{(A18-1)}$$

with

ET_o , reference evapotranspiration (mm day^{-1}) ;

Δ, slope of vapour pressure curve (kPa K^{-1})

R_n, net radiation at the crop surface (MJ m^{-2} day^{-1}) ;

G, soil heat flux density (MJ m^{-2} day^{-1}) ;

T, air temperature at 2 m height (°C) ;

e_s, saturation vapour pressure (kPa) ;

e_a, actual vapour pressure (kPa) ;

u_2, wind speed at 2 m height (m s^{-1}) ;

γ, the psychometric constraint (kPa K^{-1}) ;

where G was set equal to 0.

The following subparameterisation was used for the saturation vapour pressure (Equations 11 and 12 from Allen et al., 1998)

$$e_s = \frac{e^0(T_{max}) + e^0(T_{min})}{2}$$ (A18-2)

with

$$e^0(T) = 0.6108 \exp\left(\frac{17.27T}{T + 237.3}\right)$$ (A18-3)

with

$e^0(T)$, saturation vapour pressure at the air temperature T (kPa) ;

T, air temperature (°C) ;

T_{max}, maximum daily air temperature (°C) ;

T_{min}, minimum daily air temperature (°C) .

The slope of the vapour pressure curve was estimated from (Equation 13 of Allen et al., 1998) :

$$\Delta = \frac{4096\left(0.6108 \exp\left(\frac{17.27T}{T + 237.3}\right)\right)}{(T + 237.3)^2}$$ (A18-4)

The psychrometric constant was estimated from Equation 8 of Allen et al. (1998):

$$\gamma = 0.665 \cdot 10^{-3} P$$ (A18-5)

with

P, the atmospheric pressure (kPa).

This atmospheric pressure was estimated from the elevation above sea level using Equation 7 of Allen et al. (1998).

The wind speed at 2 m was estimated from the wind speed at 10 m (i.e. the measurement height in the MARS database) using Equation 47 of Allen et al. (1998). This implies that the wind speed at 2 m is 0.75 times the wind speed at 10 m.

The net radiation R_n was calculated as the difference between the net shortwave radiation R_{ns} and the outgoing net longwave radiation R_{nl} (Equation 40 of Allen et al., 1998).

$$R_{nl} = \sigma\left(\frac{T_{max,K}^4 + T_{min,K}^4}{2}\right)\left(0.34 - 0.14\sqrt{e_a}\right)\left(1.35\frac{R_s}{R_{so}} - 0.35\right)$$ (A18-6)

with

R_{nl}, net outgoing longwave radiation (MJ m^{-2} day^{-1})

σ, Stephan-Boltzman constant (4.903 10^{-9} MJ K^{-4} m^{-2} day^{-1})

$T_{max,K}$, maximum absolute temperature during the 24 hours day (K)

$T_{min,K}$, maximum absolute temperature during the 24 hours day (K)

R_s, measured incoming solar radiation (MJ m^{-2} day^{-1})

R_{so}, calculated clear sky radiation (MJ m^{-2} day^{-1})

The last term of this equation (1.35 R_s/R_{so} - 0.35) expresses the effect of cloudiness. Allen et al. (1998) prescribe that R_s/R_{so} has to be less than or equal to 1.0. The clear sky radiation R_{so} is estimated from the elevation above sea level and the extraterrestrial radiation, R_a, using Equation 37 of Allen et al. (1998). This extraterrestrial radiation is estimated from the day-month-year combination and the latitude of the location (provided in Table A20-37) using Equations 21, 22, 23, 24 and 25 of Allen et al. (1998).

The net shortwave radiation was calculated as:

$$R_{ns} = (1 - \alpha)R_s \qquad\qquad\qquad\qquad (A18-7)$$

where the albedo α (-) was set to 0.23 (Equation 38 of Allen et al., 1998).

The elevation above sea level of all nine locations was assumed to be 100 m above sea level. Further input for the calculations were daily values of T_{max}, T_{min}, incoming solar radiation R_s, wind speed at 10 m, and actual vapour pressure, e_a.

Selection of ET0 approach

Table A18-1 illustrates the differences between the two methods.

Table A18-1. Differences between reference evapotranspiration (mm) using the FAO and MARS approaches.

Location	ET Type	Mean	Maximum	Minimum
Châteaudun	FAO	2.12	9.06	-0.05
	MARS	2.03	8.44	0.00
Hamburg	FAO	1.68	7.01	-0.64
	MARS	1.68	6.98	0.00
Jokioinen	FAO	1.43	6.21	-1.55
	MARS	1.53	6.51	0.00
Kremsmünster	FAO	1.84	7.28	-0.22
	MARS	1.84	6.83	0.00
Okehampton	FAO	1.84	8.15	-0.54
	MARS	1.94	7.95	0.00
Piacenza	FAO	2.21	7.56	-0.09
	MARS	2.11	7.41	0.00
Porto	FAO	2.62	10.40	-0.04
	MARS	2.41	9.59	0.00
Sevilla	FAO	4.09	13.65	-0.01
	MARS	3.57	12.86	0.00
Thiva	FAO	3.28	11.41	0.33
	MARS	2.81	10.00	0.02

Some observations resulting from the comparison of the two data sets are:

- For the ET0_MARS dataset for Sevilla, a relatively large number of zero ET0 values are available that do not correlate with low ET0 values in the ET0_FAO data set for Sevilla. This is an indication of erroneous data entries in the ET0_MARS dataset for Sevilla.

- Some negative ET0 results are obtained for ET0_FAO for all scenarios except Thiva, and these negative values are significant for the Northern European scenarios. This is the result of the procedure that is used to obtain daily averages of the vapour pressure and saturated vapour pressure. At days for which a negative ET0 was calculated, the daily averaged saturated vapour pressure, which was calculated from the minimum and maximum temperature using Equation A18-2 and A18-3, was smaller than the daily averaged vapour pressure that was calculated from measurements. Noted that this occurred usually when minimum temperatures were below 0°C and maximum temperatures above 0°C. Th is occurs because Equation A18-3 is not exact for temperatures below 0°C sinc e the slope of the saturated vapour curve is discontinuous at the melting point, whereas the slope of Equation A18-3 is continuous (see Equation A18-4).

- The ET0_FAO is usually higher than ET0_Mars. In two stations, Thiva and Sevilla, the mean ETO is about 15 percent of the mean ET0_Mars. In three stations, Porto, Piacenza, and Châteaudun, this difference is between 4 and 10 percent of the mean ET0_Mars. In the four 'northern' European stations, Okehampton, Kremsmünster, Hamburg and Jokioinen, the mean ET0_Mars is equal to or smaller than the mean ET0 (for Jokioinen even 7 percent smaller).
- The ET0_FAO parameterization is considered to be more reliable for southern European conditions since it was developed to support irrigation water management. For semi-arid conditions, which prevail in Thiva and Sevilla, the ET0_FAO parameterization even tends to underestimate the reference evapotranspiration (Dirk Raes, K.U. Leuven, Belgium, personal communication). Therefore, the ET0_Mars is considered to underestimate the actual reference evapotranspiration in southern European countries.

Based on the information in this section the work group decided to use the FAO procedures for calculating reference evapotranspiration for Porto, Piacenza, Châteaudun, Thiva, and Sevilla. The MARS approach to calculating reference evapotranspiration will be retained for the other four northern European locations (Okehampton, Kremsmünster, Hamburg and Jokioinen) because there was little difference between the two approaches for these climatic conditions and the parameterisation procedure proposed by the FAO sometimes leads to negative reference evapotranspiration rates in northern European conditions.

As described before, the FAO procedure resulted sometimes in small negative values for Porto, Piacenza, Châteaudun, and Sevilla (see Table A18-1). These were set to zero in the meteorological input files of the leaching models because negative values are not considered realistic and because these leaching models do not accept negative reference evapotranspiration values.

References

Allen RG, Pereira LS, Raes D and Smith M. 1998. Crop evapotranspiration - Guidelines for computing crop water requirements. FAO Irrigation and drainage paper 56. FAO, Rome. Available at www.fao.org/docrep/X0490E/x0490e00.htm#Contents.

APPENDIX 19. PROCEDURES FOR ESTIMATING CROP EVAOPOTRANSPIRATION FACTORS

A comparison of the evapotranspiration showed that the different procedures within the models for implementing crop kc factors were contributing significantly to the variability of the overall water balance. Therefore the work group decided to harmonize the procedures by implementing a common procedure in which the year was divided into four periods. The cropping data from FOCUS (2000) as well as the length of the senescence period from (Doorenbos and Pruitt, 1977; and Raes et al. 1988) was used to define these periods. The kc values were based on information from Doorenbos and Pruitt (1977) and Raes et al. (1988). The resulting time periods and kc factors are included in the tables in Appendix 20. The following paragraphs describe the derivation of the kc factors.

Four each of the four periods the kc was assigned in the following manner:

Harvest to the day before emergence. The soil surface is bare soil and the kc factor was assumed to be 1.0 as in FOCUS (2000).

Emergence to the day before maximum LAI (leaf area index). The kc for this period was the average of the kc at the time of emergence (value of 1) and the kc at maximum LAI.

Maximum LAI to day before start of senescence. The kc for this period was the kc at maximum LAI.

Start of senescence to the day before harvest. The kc for this period was the average of the kc at maximum LAI and the kc at senescence.

Special Cases:

Apples. Emergence was considered to be leaf emergence and harvest was considered to be the time of leaf drop.

Bush berries. The kc factors provided for vines were used.

Citrus. A year-round kc value of 0.60 was assumed.

Grass and alfalfa. A year-round kc value of 1 was assumed.

Strawberries. A kc value of 1 was assumed based on expert judgement and some informal information found on the internet.

Senescence date before maximum LAI date. When the start of senescence, calculated by subtracting the length of the senescence period from the harvest date, was prior to day of maximum LAI provided by local experts, senescence was considered to start on the day of maximum LAI and the period starting at maximum LAI until the day before the start of senescence was eliminated.

Emergence data of March 1. Emergence dates of March 1 were changed to March 2 to avoid that the day before emergence varied between February 28 and 29.

References

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2, 202pp.

Doorenbos and Pruitt. 1997. Crop water requirements. FAO, Irrigation and drainage paper 24, Rome, 144 pp.

Raes D, H. Lemmens, P. Van Aelst, M. Vanden Bulcke and M. Smith. 1988. IRSIS, Irrigation scheduling information system. V1, Manual. Lab. of land management, KU Leuven.

APPENDIX 20. DEFINITION OF THE FOCUS SCENARIOS

Definition of the Châteaudun Scenarios

Table A20-1. Crop parameters for Châteaudun.

| Crop | Growth Stage | | | | Max. LAI | | Root Depth |
	Planting (dd/mm)	Emergence (dd/mm)	Senescence (dd/mm)	Harvest (dd/mm)	$(m^2\ m^{-2})$	(dd/mm)	(m)
apples	perennial	01/04[@]	01/09	01/10[#]	4	31/05	1.0
grass + alfalfa	perennial[$]	01/04	NA	15/05	5	15/05	0.5
		16/05		30/06	5	30/06	0.5
		01/07		15/08	5	15/08	0.5
		16/08		30/09	5	30/09	0.5
potatoes	15/04	30/04	02/08	01/09	4	15/06	0.6
sugar beets	25/03	16/04	05/09	15/10	5	15/07	1.0
winter cereals	20/10	26/10*	20/06	15/07	7.5	31/05	0.8
cabbage		20/04[&]	20/06	15/07	3	31/05	0.6
		31/07[&]	30/09	15/10	3	05/09	0.6
carrots	28/02	10/03	01/05	31/05	3	20/04	0.8
	30/06	10/07	21/08	20/09	3	10/08	0.8
maize	20/04	01/05	01/09	01/10	4.5	15/08	0.8
oil seed rape (win)	30/08	07/09**	10/06	10/07	4	20/04	1.0
onions	15/04	25/04	18/07	01/09	3	30/06	0.6
peas (animals)	25/03	05/04	31/07	15/08	4	07/06	0.6
spring cereals	20/02	10/03	30/06	20/07	5	10/06	0.6
tomatoes		10/05[&]	26/07	25/08	6	30/06	0.8
vines	perennial	01/04	13/08	01/11	6	31/07	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth

& transplanted from seedbed - date indicates day of transplantation.

* spring point of 15/4. See Section 11.5.1.2.

** spring point of 11/3. See Section 11.5.1.2.

Table A20-2. Crop Kc factors for Châteaudun.

| Crop | Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm) | | | | | | | |
| | Harvest to Emergence | | Emergence to Maximum LAI | | Maximum LAI to Senescence | | Senescence to Harvest | |
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	01/10-31/03	1.00	01/04-30/05	1.05	31/05-31/08	1.10	01/09-30/09	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	01/09-29/04	1.00	30/04-14/06	1.05	15/06-01/08	1.10	02/08-31/08	0.90
sugar beets	15/10-15/04	1.00	16/04-14/07	1.05	15/07-04/09	1.10	05/09-14/10	0.85
winter cereals	15/07-25/10	1.00	26/10-30/05	1.05	31/05-19/06	1.10	20/06-14/07	0.70
cabbage	15/10-19/04 15/07-30/07	1.00	20/04-30/05 31/07-04/09	1.00	31/05-19/06 05/09-29/09	1.00	20/06-14/07 30/09-14/10	0.93
carrots	20/09-09/03 31/05-09/07	1.00	10/03-19/04 10/07-09/08	1.03	20/04-30/04 10/08-20/08	1.05	01/05-30/05 21/08-19/09	0.90
maize	01/10-30/04	1.00	01/05-14/08	1.05	15/08-31/08	1.10	01/09-30/09	0.83
oil seed rape (win)	10/07-06/09	1.00	07/09-19/04	1.00	20/04-09/06	1.00	10/06-09/07	0.93
onions	01/09-24/04	1.00	25/04-29/06	0.98	30/06-17/07	0.95	18/07-31/08	0.85
peas (animals)	15/08-04/04	1.00	05/04-06/06	1.05	07/06-30/07	1.10	31/07-14/08	1.05
spring cereals	20/07-09/03	1.00	10/03-09/06	1.05	10/06-29/06	1.10	30/06-19/07	0.70
tomatoes	25/08-09/05	1.00	10/05-29/06	1.05	30/06-25/07	1.10	26/07-24/08	0.85
vines	01/11-31/03	1.00	01/04-30/07	0.88	31/07-12/08	0.75	13/08-31/10	0.65

Table A20-3. Soil parameters for Châteaudun.

| Horizon | Depth (cm) | Classification | pH-H_2O[*] | pH-KCl[†] | Texture (µm) | | | om (%) | oc (%) | Bulk Density (g cm^{-3}) | Depth Factor[@] |
					<2	2-50	>50				
Ap	0-25	silty clay loam	8.0	7.3	30	67	3	2.4	1.39	1.3	1.0
B1	25-50	silty clay loam	8.1	7.4	31	67	2	1.6	0.93	1.41	0.5
B2	50-60	silt loam	8.2	7.5	25	67	8	1.2	0.7	1.41	0.5
II C1	60-100	limestone[#]	8.5	7.8	26	44	30	0.5	0.3	1.37	0.3
II C1	100-120	limestone[#]	8.5	7.8	26	44	30	0.5	0.3	1.37	0
II C2	120-190	limestone[#]	8.5	7.8	24	38	38	0.46	0.27	1.41	0
M	190-260	limestone[#]	8.3	7.6	31	61	8	0.36	0.21	1.49	0

[#] The limestone is cryoturbated in the C-horizons and powdery in the M-horizon.

[*] Measured at a soil solution ratio of 1:5

[†] These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[@] The depth factor indicates the relative transformation rate in the soil layer.

The profile is overlying an aquitanian limestone. The depth of the ground water table is around 12 m.

Table A20-4. Soil hydraulic properties for Châteaudun, Van Genuchten/Mualem parameters (restricted form, m=1-1/n).

Depth (cm)	θ_s (m³ m⁻³)	θ_r (m³ m⁻³)	α (m⁻¹)	n	Water Content		Ksat (m s⁻¹*10⁻⁶)	λ	AW[@] (mm)
					10kPa (m³ m⁻³)	1600kPa (m³ m⁻³)			
0-25	0.43	0.0	5.00	1.080	0.374	0.253	20.00	0.50	30.25
25-50	0.44	0.0	5.00	1.095	0.372	0.235	30.00	0.50	34.25
50-60	0.44	0.0	5.00	1.095	0.372	0.235	50.00	2.50	13.70
60-100	0.44	0.0	1.50	1.160	0.386	0.185	12.00	-2.00	80.40
100-120	0.44	0.0	1.50	1.160	0.386	0.185	12.00	-2.00	-
120-190	0.49	0.0	1.07	1.280	0.417	0.116	9.06	-1.50	-
190-260	0.42	0.0	1.91	1.152	0.362	0.176	14.81	-1.18	-

[@] Plant available water in the soil layer.

Plant available water in the top 1 m is 158.6 mm.

For the MACRO model a few additional parameters are needed. These are obtained from the same original dataset. In order to avoid confusion these parameters are not included here.

Definition of the Hamburg Scenarios

Table A20-5. Crop parameters for Hamburg.

| Crop | Growth Stage | | | | Max. LAI | | Root Depth (m) |
	Planting (dd/mm)	Emergence (dd/mm)	Senescence (dd/mm)	Harvest (dd/mm)	(m^2 m^{-2})	(dd/mm)	
apples	perennial	15/04[@]	30/09	30/10[#]	4	01/07	1.0
grass + alfalfa	perennial	25/03[$]	NA	31/05	5	31/05	0.6
		01/06		15/07	5	15/07	0.6
		16/07		31/08	5	31/08	0.6
potatoes	01/05	10/05	16/08	15/09	3	20/07	0.7
sugar beets	01/04	15/04	08/09	08/10	4.2	30/08	1.0
winter cereals	12/10	01/11*	16/07	10/08	3.8	01/06	1.0
beans (field)	25/03	10/04	05/08	25/08	4	10/07	0.9
cabbage		20/04[&]	30/06	15/07	3	31/05	0.7
		31/07[&]	30/09	15/10	3	05/09	0.7
carrots	28/02	10/03	01/05	31/05	3	20/04	0.8
	30/06	10/07	21/08	20/09	3	10/08	0.8
maize	20/04	05/05	21/08	20/09	4.2	30/07	1.0
oil seed rape (win)	25/08	02/09**	28/06	28/07	4	05/05	1.0
onions	15/04	25/04	18/07	01/09	3	30/06	0.7
peas (animals)	25/03	10/04	10/08	25/08	4	10/07	0.9
spring cereals	10/03	01/04	31/07	20/08	3.9	05/06	0.9
strawberries	perennial	15/03	01/08	31/08^	2.5	30/04	0.7
vines	perennial	01/05	11/08	30/10	3	15/07	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

^ crop removed from field.

* spring point of 4/5 See Section 11.5.1.2.

** spring point of 18/4. See Section 11.5.1.2.

Table A20-6. Crop Kc factors for Hamburg.

Crop	Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm)							
	Harvest to Emergence		Emergence to Maximum LAI		Maximum LAI to Senescence		Senescence to Harvest	
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	30/10-14/04	1.00	15/04-30/06	1.05	01/07-29/09	1.10	30/09-29/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	15/09-09/05	1.00	10/05-19/07	1.05	20/07-15/08	1.10	16/08-14/09	0.90
sugar beets	08/10-14/04	1.00	15/04-29/08	1.05	30/08-07/09	1.10	08/09-07/10	0.85
winter cereals	10/08-31/10	1.00	01/11-05/31	1.05	01/06-15/07	1.10	16/07-09/08	0.70
beans (field)	25/08-09/04	1.00	10/04-09/07	1.05	10/07-04/08	1.10	05/08-24/08	0.70
cabbage	15/10-19/04 15/07-30/07	1.00	20/04-30/05 31/07-04/09	1.00	31/05-29/06 05/09-29/09	1.00	30/06-14/07 30/09-15/10	0.93
carrots	20/09-09/03 31/05-09/07	1.00	10/03-19/04 10/07-09/08	1.03	20/04-4/30 10/08-20/08	1.05	01/05-30/05 21/08-19/09	0.90
maize	20/09-04/05	1.00	05/05-29/07	1.05	30/07-20/08	1.10	21/08-19/09	0.83
oil seed rape (win)	28/07-01/09	1.00	02/09-04/05	1.00	05/05-27/06	1.00	28/06-27/07	0.93
onions	01/09-24/04	1.00	25/04-29/06	0.98	30/06-17/07	0.95	18/07-31/08	0.85
peas (animals)	25/08-09/04	1.00	10/04-09/07	1.05	10/07-09/08	1.10	10/08-24/08	1.05
spring cereals	20/08-31/03	1.00	01/04-04/06	1.05	05/06-30/07	1.10	31/07-19/08	0.70
strawberries	31/08-14/03	1.00	15/03-29/04	1.00	30/04-7/31	1.00	01/08-30/08	1.00
vines	30/10-30/04	1.00	01/05-14/07	0.88	15/07-10/08	0.75	11/08-29/10	0.65

Table A20-7. Soil parameters for Hamburg.

Horizon	Depth (cm)	Classification	pH-H_2O*	pH-KCl[†]	Texture (µm)			om (%)	oc (%)	Bulk Density (g cm⁻³)	Depth Factor[@]
					<2	2-50	>50				
Ap	0-30	sandy loam	6.4	5.7	7.2	24.5	68.3	2.6	1.5	1.5	1.0
BvI	30-60	sandy loam	5.6	4.9	6.7	26.3	67	1.7	1	1.6	0.5
BvII	60-75	sand	5.6	4.9	0.9	2.9	96.2	0.34	0.2	1.56	0.3
Bv/Cv	75-90	sand	5.7	5	0	0.2	99.8	0	0	1.62	0.3
Cv	90-100	sand	5.5	4.8	0	0	100	0	0	1.6	0.3
Cv	100-200	sand	5.5	4.8	0	0	100	0	0	1.6	0.0

[†] These values are estimated from the measured KCl values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

* Measured at a soil solution ratio of 1:2.5

[@] The depth factor indicates the relative transformation rate in the soil layer.

Ground water depth of 2 m (estimated by IUCT).

Table A20-8. Soil hydraulic properties for Hamburg, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m³ m⁻³)	θ_r (m³ m⁻³)	α (m⁻¹)	n	m	Water Content 10kPa (m³ m⁻³)	Water Content 1600kPa (m³ m⁻³)	Ksat (m s⁻¹*10⁻⁶)	λ	AW[@] (mm)
0-30	0.3910	0.0360	1.491	1.4680	0.3188	0.292	0.064	23.330	0.500	68.4
30-60	0.3700	0.0300	1.255	1.5650	0.3610	0.277	0.047	31.670	0.500	69.0
60-75	0.3510	0.0290	1.808	1.5980	0.3742	0.229	0.040	28.330	0.500	28.4
75-90	0.3100	0.0150	2.812	1.6060	0.3773	0.163	0.022	28.330	0.500	21.2
90-100	0.3100	0.0150	2.812	1.6060	0.3773	0.163	0.022	28.330	0.500	14.1
100-200	0.3100	0.0150	2.812	1.6060	0.3773	0.163	0.022	28.330	0.500	

[@] Plant available water in the soil layer.

Plant available water in the top 1 m is 201 mm.

Definition of the Jokioinen Scenarios

Table A20-9. Crop parameters for Jokioinen.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m² m⁻²)	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	10/05[@]	15/09	15/10[#]	4	25/05	1.0
grass + alfalfa	perennial[$]	15/04[$]	NA	15/06	7	15/06	0.9
		16/06		15/07	7	15/07	0.9
		16/07		25/08	7	25/08	0.9
potatoes	15/05	05/06	05/09	25/09	5	30/08	0.6
sugar beets	10/05	25/05	05/09	15/10	5	10/08	0.9
winter cereals	10/09	20/09*	21/07	15/08	4.8	25/06	0.95
bush berries	perennial	10/05	06/08	25/10	4	25/05	0.6
cabbage		20/05[&]	05/09	20/09	5	05/09	0.9
carrots	15/05	01/06	05/09	05/10	4	05/09	0.6
oil seed rape (sum)	10/05	20/05	31/07	30/08	3.8	05/07	0.8
onions	10/05	20/05	01/07	15/08	4	25/06	0.3
peas (animals)	10/05	25/05	10/08	25/08	4	30/06	0.8
spring cereals	07/05	18/05	05/08	25/08	4.5	30/06	0.8
strawberries	perennial	15/05	16/08	15/09^	2.5	25/06	0.3

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

^ crop removed from field.

* spring point of 14/5 See Section 11.5.1.2.

Table A20-10. Crop Kc factors for Jokioinen.

| Crop | Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm) | | | | | | | |
| | Harvest to Emergence | | Emergence to Maximum LAI | | Maximum LAI to Senescence | | Senescence to Harvest | |
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	15/10-09/05	1.00	10/05-24/05	1.05	25/05-14/09	1.10	15/09-14/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	25/09-04/06	1.00	05/06-29/08	1.05	30/08-04/09	1.10	05/09-24/09	0.90
sugar beets	15/10-24/05	1.00	25/05-09/08	1.05	10/08-04/09	1.10	05/09-14/10	0.85
winter cereals	15/08-19/09	1.00	20/09-24/06	1.05	25/06-20/07	1.10	21/07-14/08	0.70
bush berries	25/10-09/05	1.00	10/05-24/05	0.88	25/05-05/08	0.75	06/08-24/10	0.65
cabbage	20/09-19/05	1.00	20/05-04/09	1.00			05/09-19/09	0.93
carrots	05/10	1.00	01/06-04/09	1.03			05/09-04/10	0.95
oil seed rape (sum)	30/08-19/05	1.00	20/05-04/07	1.00	05/07-30/07	1.00	31/07-29/08	0.93
onions	15/08-19/05	1.00	20/05-24/06	0.98	25/06-30/06	0.95	01/07-14/08	0.85
peas (animals)	25/08-24/05	1.00	25/05-29/06	1.05	30/06-09/08	1.10	10/08-24/08	1.05
spring cereals	25/08-17/05	1.00	18/05-29/06	1.05	30/06-04/08	1.10	05/08-24/08	0.70
strawberries	15/09-14/05	1.00	15/05-24/06	1.00	25/06-15/08	1.00	16/08-14/09	1.00

Table A20-11. Soil parameters for Jokioinen.

| Horizon | Depth (cm) | Classification | pH-H$_2$O[*] | pH-KCl[†] | Texture (µm) | | | om (%) | oc (%) | Bulk Density (g cm^{-3}) | Depth Factor[@] |
					<2	2-50	>50				
Ap	0-30	loamy fine sand	6.2	5.5	3.6	23.2	73.2	7.0	4.06	1.29	1.0
Bs	30-60	loamy fine sand	5.6	4.9	1.8	12.2	86.0	1.45	0.84	1.52	0.5
BC1	60-95	loamy fine sand	5.4	4.7	1.2	14.9	83.9	0.62	0.36	1.64	0.3
BC2	95-100	loamy fine sand	5.4	4.7	1.7	18.9	79.4	0.50	0.29	1.63	0.3
BC2	100-120	loamy fine sand	5.4	4.7	1.7	18.9	79.4	0.50	0.29	1.63	0.0
Cg	120-150	fine sand	5.3	4.6	1.9	8.6	89.5	0.36	0.21	1.66	0.0

[*] Measured at a soil solution ratio of 1:2.5

[†] These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[@] The depth factor indicates the relative transformation rate in the soil layer.

The ground water level is approximately 1.52 m below soil surface.

Table A20-12. Soil hydraulic properties for Jokioinen, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m³ m⁻³)	θ_r (m³ m⁻³)	α (m⁻¹)	n	m	Water Content 10kPa (m³ m⁻³)	Water Content 1600kPa (m³ m⁻³)	Ksat (m s⁻¹*10⁻⁶)	λ	AW[@] (mm)
0-30	0.4519	0.0100	3.900	1.2745	0.2154	0.304	0.086	4.165	-0.646	65.4
30-60	0.3890	0.0100	6.650	1.4849	0.3266	0.158	0.023	5.686	-0.060	40.5
60-95	0.3632	0.0100	6.000	1.5007	0.3336	0.151	0.021	4.294	0.833	45.5
95-100	0.3636	0.0100	5.600	1.4778	0.3233	0.162	0.024	4.142	0.957	6.9
100-120	0.3636	0.0100	5.600	1.4778	0.3233	0.162	0.024	4.142	0.957	
120-150	0.3432	0.0100	7.250	1.5472	0.3537	0.121	0.017	4.834	1.036	

[@] Plant available water in the soil layer.

Plant available water in top meter is 158.3 mm.

Definition of the Kremsmünster Scenarios

Table A20-13. Crop parameters for Kremsmünster.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m² m⁻²)	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	15/04[@]	30/09	30/10[#]	4	01/07	1.0
grass + alfalfa	perennial	10/04[$]	NA	25/05	5	25/05	0.5
		26/05		15/07	5	15/07	0.5
		16/07		20/09	5	20/09	0.5
potatoes	01/05	10/05	16/08	15/09	3.5	20/07	0.7
sugar beets	01/04	15/04	31/08	10/10	4.2	30/08	1.0
winter cereals	25/10	05/11*	16/07	10/08	4	05/06	1.0
beans (field)	25/03	10/04	05/08	25/08	4	10/07	0.8
cabbage		20/04[&]	30/06	15/07	3	31/05	0.6
		31/07[&]	30/09	15/10	3	05/09	0.6
carrots	28/02	10/03	01/05	31/05	3	20/04	0.7
	30/06	10/07	21/08	20/09	3	10/08	0.7
maize	20/04	05/05	21/08	20/09	4.2	30/07	1.0
oil seed rape (win)	25/08	02/09**	28/06	28/07	4	05/05	1.0
onions	15/04	25/04	18/07	01/09	3	30/06	0.6
spring cereals	10/03	01/04	31/07	20/08	3.9	05/06	0.9
strawberries	perennial	15/03	01/08	31/08^	2.5	30/04	0.7
vines	perennial	01/05	11/08	30/10	3	15/07	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

^ crop removed from field.

* spring point of 24/4 See Section 11.5.1.2.

** spring point of 15/4. See Section 11.5.1.2.

Table A20-14. Crop Kc factors for Kremsmünster.

| Crop | Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm) | | | | | | | |
| | Harvest to Emergence | | Emergence to Maximum LAI | | Maximum LAI to Senescence | | Senescence to Harvest | |
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	30/10-14/04	1.00	15/04-30/06	1.05	01/07-29/09	1.10	30/09-29/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	15/09-09/05	1.00	10/05-19/07	1.05	20/07-15/08	1.10	16/08-14/09	0.90
sugar beets	10/10-14/04	1.00	15/04-29/08	1.05	30/08	1.10	31/08-09/10	0.85
winter cereals	10/08-04/11	1.00	05/11-04/06	1.05	05/06-15/07	1.10	16/07-09/08	0.70
beans (field)	25/08-09/04	1.00	10/04-09/07	1.05	10/07-04/08	1.10	05/08-24/08	0.70
cabbage	15/10-19/04 15/07-30/07	1.00	20/04-30/05 31/07-04/09	1.00	31/05-29/06 05/09-29/09	1.00	30/06-14/07 30/09-14/10	0.93
carrots	20/09-09/03 31/05-09/07	1.00	10/03-19/04 10/07-09/08	1.03	20/04-30/04 10/08-20/08	1.05	01/05-30/05 21/08-19/09	0.90
maize	20/09-04/05	1.00	05/05-29/07	1.05	30/07-20/08	1.10	21/08-19/09	0.83
oil seed rape (win)	28/07-01/09	1.00	02/09-04/05	1.00	05/05-27/06	1.00	28/06-27/07	0.93
onions	01/09-24/04	1.00	25/04-29/06	0.98	30/06-17/07	0.95	18/07-31/08	0.85
spring cereals	20/08-31/03	1.00	01/04-04/06	1.05	05/06-30/07	1.10	31/07-19/08	0.70
strawberries	31/08-14/03	1.00	15/03-29/04	1.00	30/04-31/07	1.00	01/08-30/08	1.00
vines	30/10-30/04	1.00	01/05-14/07	0.88	15/07-10/08	0.75	11/08-29/10	0.65

Table A20-15. Soil parameters for Kremsmünster.

| Depth (cm) | Classification | pH-H$_2$O[*] | pH-KCl[†] | Texture (μm) | | | om (%) | oc (%) | Bulk Density (g cm^{-3}) | Depth Factor[@] |
				<2	2-50	>50				
0-30	loam/silt loam	7.7	7.0	14	50	36	3.6	2.1	1.41	1.0
30-50	loam/silt loam	7.0	6.3	25	50	25	1.0	0.6	1.42	0.5
50-60	loam/clay loam	7.1	6.4	27	44	29	0.5	0.3	1.43	0.5
60-100	loam/clay loam	7.1	6.4	27	44	29	0.5	0.3	1.43	0.3
100-200	loam/clay loam	7.1	6.4	27	44	29	0.5	0.3	1.43	0.0

[†] These values are estimated from the measured KCl values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[*] Measured at a soil solution ratio of 1:2.5

[@] The depth factor indicates the relative transformation rate in the soil layer.

The depth of ground water is around 1.6 m, for apples and vines a deeper ground water level has to be assumed. At a depth of approximately 3.3 m a rather impermeable layer is present.

Layer below 1 m copied from 60 - 100 cm layer.

Layer 0 - 30 cm is Ap horizon, 30 - 100 cm is Bwg horizon.

Table A20-16. Soil hydraulic properties for Kremsmünster, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m³ m⁻³)	θ_r (m³ m⁻³)	α (m⁻¹)	n	m	Water Content 10kPa (m³ m⁻³)	Water Content 1600kPa (m³ m⁻³)	Ksat (m s⁻¹*10⁻⁶)	λ	AW[@] (mm)
0-30	0.4246	0.0100	2.440	1.2186	0.1794	0.334	0.123	1.769	-2.080	63.3
30-50	0.4446	0.0100	2.700	1.1659	0.1423	0.365	0.169	2.780	-2.404	39.2
50-60	0.4430	0.0100	3.080	1.1578	0.1363	0.361	0.173	2.459	-2.065	18.8
60-100	0.4430	0.0100	3.080	1.1578	0.1363	0.361	0.173	2.459	-2.065	75.2
100-200	0.4430	0.0100	3.080	1.1578	0.1363	0.361	0.173	2.459	-2.065	

[@] Plant available water in soil layer.

Plant available water in top meter is 196.5 mm.

Layer 100 - 200 cm copied from layer 60 - 100 cm because of lacking information.

Definition of the Okehampton Scenarios

Table A20-17. Crop parameters for Okehampton.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m² m⁻²)	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	25/03[@]	16/08	15/09[#]	2.5	15/06	1.0
grass + alfalfa	perennial	10/02[$]	NA	15/05	4.5	15/05	0.45
		16/05		15/07	4.5	15/07	0.45
		16/07		15/09	4.5	15/09	0.45
potatoes	15/04	30/04	02/08	01/09	4	15/07	0.6
sugar beets	10/04	25/04	15/09	25/10	3	30/08	0.8
winter cereals	07/10	17/10*	07/07	01/08	7.5	15/05	0.8
beans (field)	01/03	15/03	26/08	15/09	4	07/06	0.45
linseed	25/03	30/03	18/08	25/09	3	25/06	0.6
maize	07/05	25/05	18/08	07/10	7	15/07	0.8
oil seed rape (sum)	25/03	30/03	21/07	20/08	3	15/05	0.6
oil seed rape (win)	07/08	14/08**	21/06	21/07	4.5	30/04	0.85
peas (animals)	25/03	05/04	31/07	15/08	4.0	07/06	0.45
spring cereals	25/03	01/04	31/07	20/08	4.5	22/05	0.6

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

* spring point of 21/4 See Section 11.5.1.2.

** spring point of 9/4. See Section 11.5.1.2.

Table A20-18. Crop Kc factors for Okehampton.

Crop	Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm)							
	Harvest to Emergence		Emergence to Maximum LAI		Maximum LAI to Senescence		Senescence to Harvest	
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	15/09-24/03	1.00	25/03-14/06	1.05	15/06-15/08	1.10	16/08-14/09	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	01/09-29/04	1.00	30/04-14/07	1.05	15/07-01/08	1.10	02/08-31/08	0.90
sugar beets	25/10-24/04	1.00	25/04-29/08	1.05	30/08-14/09	1.10	15/09-24/10	0.85
winter cereals	01/08-16/10	1.00	17/10-14/05	1.05	15/05-06/07	1.10	07/07-31/07	0.70
beans (field)	15/09-14/03	1.00	15/03-06/06	1.05	07/06-25/08	1.10	26/08-14/09	0.70
linseed	25/0929/03	1.00	30/03-24/06	1.03	25/06-17/08	1.05	18/08-24/09	0.65
maize	07/10-24/05	1.00	25/05-14/07	1.05	15/07-17/08	1.10	18/08-06/10	0.83
oil seed rape (sum)	20/08-29/03	1.00	30/03-14/05	1.00	15/05-20/07	1.00	21/07-19/08	0.93
oil seed rape (win)	21/07-13/08	1.00	14/08-29/04	1.00	30/04-20/06	1.00	21/06-20/07	0.93
peas (animals)	15/08-04/04	1.00	05/04-06/06	1.05	07/06-30/07	1.10	31/07-14/08	1.05
spring cereals	20/08-31/03	1.00	01/04-21/05	1.05	22/05-30/07	1.10	31/07-19/08	0.70

Table A20-19. Soil parameters for Okehampton.

Horizon	Depth (cm)	Classification	pH-H_2O*	pH-KCl[†]	Texture (µm)			om (%)	oc (%)	Bulk Density (g cm^{-3})	Depth Factor[@]
					<2	2-50	>50				
A	0-25	loam	5.8	5.1	18	43	39	3.8	2.2	1.28	1.0
Bw1	25-55	loam	6.3	5.6	17	41	42	1.2	0.7	1.34	0.5
BC	55-85	sandy loam	6.5	5.8	14	31	55	0.69	0.4	1.42	0.3
C	85-100	sandy loam	6.6	5.9	9	22	69	0.17	0.1	1.47	0.3
C	100-150	sandy loam	6.6	5.9	9	22	69	0.17	0.1	1.47	0.0

* Measured at a soil solution ratio of 1:2.5

[†] These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[@] The depth factor indicates the relative transformation rate in the soil layer.

The depth of ground is about 20 m.

Table A20-20. Soil hydraulic properties for Okehampton, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m^3 m^{-3})	θ_r (m^3 m^{-3})	α (m^{-1})	n	m	Water Content 10kPa (m^3 m^{-3})	Water Content 1600kPa (m^3 m^{-3})	Ksat (m s^{-1}*10^{-6})	λ	AW[@] (mm)
0-25	0.4664	0.0100	3.550	1.1891	0.1590	0.358	0.148	3.484	-2.581	52.5
25-55	0.4602	0.0100	3.640	1.2148	0.1768	0.340	0.125	4.887	-2.060	64.5
55-85	0.4320	0.0100	4.560	1.2526	0.2017	0.290	0.090	4.838	-1.527	60.0
85-100	0.4110	0.0100	5.620	1.3384	0.2528	0.228	0.050	4.449	-0.400	26.7
100-150	0.4110	0.0100	5.620	1.3384	0.2528	0.228	0.050	4.449	-0.400	

[@] Plant available water in the soil layer.

Plant available water in top meter is 203.7 mm.

Definition of the Piacenza Scenarios

Table A20-21. Crop parameters for Piacenza.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m^2 m^{-2})	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	01/04[@]	02/09	01/11[#]	5	31/05	1.0
grass + alfalfa	perennial[$]	28/02[$]	NA	15/05	4	15/05	0.8
		16/05		15/07	4	15/07	0.8
		16/07		20/09	4	20/09	0.8
potatoes	01/04	20/04	11/08	10/09	5	01/06	0.5
sugar beets	01/03	20/03	27/07	15/09	4	30/06	0.8
winter cereals	25/11	01/12*	01/06	01/07	7	10/05	1.0
citrus	perennial	evergreen	NA	NA	5	31/05	1.0
maize	30/04	15/05	30/09	30/10	5	31/07	1.0
oil seed rape (win)	30/09	05/10**	21/05	20/06	3.5	15/04	0.6
soybean	25/04	10/05	10/09	05/10	6.5	31/07	0.6
sunflower	01/04	20/04	26/08	20/09	4	20/06	1.0
tobacco		20/05[&]	25/09	05/10	4	20/07	1.0
tomatoes		10/05[&]	26/07	25/08	6	30/06	1.0
vines	perennial	01/04	13/08	01/11	6	31/07	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

* spring point of 19/3 See Section 11.5.1.2.

** spring point of 7/3. See Section 11.5.1.2.

Table A20-22. Crop Kc factors for Piacenza.

Crop	Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm)							
	Harvest to Emergence		Emergence to Maximum LAI		Maximum LAI to Senescence		Senescence to Harvest	
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	01/11-31/03	1.00	01/04-30/05	1.05	31/05-01/09	1.10	02/09-31/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	10/09-19/04	1.00	20/04-31/05	1.05	01/06-10/08	1.10	11/08-09/09	0.90
sugar beets	15/09-19/03	1.00	20/03-29/06	1.05	30/06-26/07	1.10	27/07-14/09	0.85
winter cereals	01/07-30/11	1.00	01/12-09/05	1.05	10/05-31/05	1.10	01/06-30/06	0.70
citrus	NA		NA		All year	0.60	NA	
maize	30/10-14/05	1.00	15/05-30/07	1.05	31/07-29/09	1.10	30/09-29/10	0.83
oil seed rape (win)	20/06-04/10	1.00	05/10-14/04	1.00	15/04-20/05	1.00	21/05-19/06	0.93
soybean	05/10-09/05	1.00	10/05-30/07	1.03	31/07-09/09	1.05	10/09-04/10	0.75
sunflower	20/09-19/04	1.00	20/04-19/06	1.05	20/06-25/08	1.10	26/08-19/09	0.75
tobacco	05/10-19/05	1.00	20/05-19/07	1.00	20/07-24/09	1.00	25/09-04/10	0.93
tomatoes	25/08-09/05	1.00	10/05-29/06	1.05	30/06-25/07	1.10	26/07-24/08	0.85
vines	01/11-31/03	1.00	01/04-30/07	0.88	31/07-12/08	0.75	13/08-31/10	0.65

Table A20-23. Soil parameters for Piacenza.

Horizon	Depth (cm)	Classification	pH-H_2O*	pH-KCl[†]	Texture (μm)			om (%)	oc (%)	Bulk Density (g cm^{-3})	Depth Factor[@]
					<2	2-50	>50				
Ap	0-30	loam	7	6.3	15	45	40	2.17	1.26	1.3	1.0
Ap	30-40	loam	7	6.3	15	45	40	2.17	1.26	1.3	0.5
Bw	40-60	silt loam	6.3	5.6	7	53	40	0.80	0.47	1.35	0.5
Bw	60-80	silt loam	6.3	5.6	7	53	40	0.80	0.47	1.35	0.3
2C	80-100	sand	6.4	5.7	0	0	100	0	0	1.45	0.3
2C	100-170	sand	6.4	5.7	0	0	100	0	0	1.45	0.0

* Measured at a soil solution ratio of 1:2.5

[†] These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[@] The depth factor indicates the relative transformation rate in the soil layer.

The depth of ground water is 1.5 m (range 1.30-1.70 m).

Table A20-24. Soil hydraulic properties for Piacenza, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m³ m⁻³)	θ_r (m³ m⁻³)	α (m⁻¹)	n	m	Water Content 10kPa (m³ m⁻³)	Water Content 1600kPa (m³ m⁻³)	Ksat (m s⁻¹*10⁻⁶)	λ	AW[@] (mm)
0-30	0.4622	0.0100	3.13	1.238	0.1993	0.341	0.113	4.269	-2.037	68.4
30-40	0.4622	0.0100	3.13	1.238	0.1993	0.341	0.113	4.269	-2.037	22.8
40-60	0.4543	0.0100	2.31	1.3531	0.261	0.317	0.065	6.138	0.109	50.4
60-80	0.4543	0.0100	2.31	1.3531	0.261	0.317	0.065	6.138	0.109	50.4
80-100	0.3100	0.0150	2.812	1.6060	0.3773	0.163	0.022	28.330	0.500	28.2
100-170	0.3100	0.0150	2.812	1.6060	0.3773	0.163	0.022	28.330	0.500	

[@] Plant available water in the soil layer.

Plant available water in top meter is 220.2 mm.

Definition of the Porto Scenarios

Table A20-25. Crop parameters for Porto.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m² m⁻²)	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	15/03[@]	1/09	31/10[#]	3	30/06	1.0
grass + alfalfa	perennial	28/02[$]	NA	15/05	4	15/05	0.8
		16/05		15/07	4	15/07	0.8
		16/07		20/09	4	20/09	0.8
potatoes (sum)	28/02	15/03	08/06	15/06	4	30/05	0.7
sugar beets	28/02	15/03	12/06	01/08	5	30/04	1.0
winter cereals	15/11	30/11	31/05	30/06	6.5	30/04	1.0
beans (vegetable)	28/02	10/03	11/08	31/08	4	15/05	0.5
cabbage		28/02[&]	16/06	01/07	4	15/05	0.5
		31/07[&]	31/10	15/11	4	31/08	0.5
carrots	15/02	28/02	11/05	31/05	4	01/05	0.5
	15/07	22/07	25/09	15/10	4	15/09	0.5
citrus	perennial	evergreen	NA	NA	6	31/05	1.0
maize	20/04	01/05	01/09	01/10	4.5	15/08	0.8
oil seed rape (sum)	15/03	22/03	26/07	25/08	3	31/05	0.9
oil seed rape (win)	30/08	07/09	10/06	10/07	4	20/04	1.0
onions	15/02	28/02	21/04	31/05	3.5	15/05	0.5
spring cereals	20/02	10/03	30/06	20/07	5	10/06	0.6
tomatoes		15/03[&]	01/08	31/08	5	15/06	0.5
vines	perennial	15/03	31/07	30/09	4	31/07	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

Table A20-26. Crop Kc factors for Porto.

Crop	Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm)							
	Harvest to Emergence		Emergence to Maximum LAI		Maximum LAI to Senescence		Senescence to Harvest	
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	31/10-14/03	1.00	15/03-29/06	1.05	30/06-08/31	1.10	01/09-30/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	15/06-14/03	1.00	15/03-29/05	1.05	30/05-07/06	1.10	08/06-14/06	0.90
sugar beets	01/08-15/03	1.00	15/03-29/04	1.05	30/04-11/06	1.10	12/06-31/07	0.85
winter cereals	30/06-29/11	1.00	30/11-29/04	1.05	30/04-30/05	1.10	31/05-29/06	0.70
beans (vegetable)	31/08-09/03	1.00	10/03-14/05	1.05	15/05-10/08	1.10	11/08-30/08	0.70
cabbage	15/11-27/02 01/07-30/07	1.00	28/02-14/05 31/07-30/08	1.00	15/05-15/06 31/08-30/10	1.0	16/06-30/06 31/10	0.93
carrots	15/10-27/02 31/05-21/07	1.00	28/02-30/04 22/07-14/09	1.03	01/05-10/05 15/09-24/09	1.05	11/05-30/05 25/09-14/10	0.90
citrus	NA		NA		All year	0.60	NA	
maize	01/10-30/04	1.00	01/05-14/08	1.05	15/08-31/08	1.10	01/09-30/09	0.83
oil seed rape (sum)	25/08-21/03	1.00	22/03-30/05	1.00	31/05-25/07	1.00	26/07-24/08	0.93
oil seed rape (win)	10/07-06/09	1.00	07/09-19/04	1.00	20/04-09/06	1.00	10/06-09/07	0.93
onions	31/05-27/02	1.00	28/02-14/05	0.98	15/05-20/04	0.95	21/04-30/05	0.85
spring cereals	20/07-09/03	1.00	10/03-09/06	1.05	10/06-29/06	1.10	30/06-19/07	0.70
tomatoes	31/08-14/03	1.00	15/03-14/06	1.05	15/06-31/07	1.10	01/08-30/08	0.85
vines	30/09-14/03	1.00	15/03-30/07	0.88			31/07-29/09	0.65

Table A20-27. Soil parameters for Porto.

Depth (cm)	Classification	pH-H_2O*	pH-KCl[†]	Texture (µm)			om (%)	oc (%)	Bulk Density (g cm^{-3})	Depth Factor[@]
				<2	2-50	>50				
0-35	loam	4.9	4.2	10	48	42	2.45	1.42	1.09	1.0
35-60	sandy loam	4.8	4.1	8	31	61	1.35	0.78	1.45	0.5
60-100	sandy loam	4.8	4.1	8	31	61	1.35	0.78	1.45	0.3
100-120	sandy loam	4.8	4.1	8	31	61	1.35	0.78	1.45	0.0

* Measured at a soil solution ratio of 1:2.5

[†] These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[@] The depth factor indicates the relative transformation rate in the soil layer.

Depth of ground water: summer lower than 2 m, winter 0.7 - 1.2 m.

Top layer is Ap horizon, other layers C1 horizon.

Table A20-28. Soil hydraulic properties for Porto, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m^3 m^{-3})	θ_r (m^3 m^{-3})	α (m^{-1})	n	m	Water Content 10kPa (m^3 m^{-3})	Water Content 1600kPa (m^3 m^{-3})	Ksat (m $s^{-1}*10^{-6}$)	λ	AW[@] (mm)
0-35	0.5230	0.0100	2.30	1.2888	0.2241	0.388	0.103	6.504	-1.949	99.75
35-60	0.4183	0.0100	4.29	1.3078	0.2354	0.262	0.065	4.774	-0.9972	49.25
60-100	0.4183	0.0100	4.29	1.3078	0.2354	0.262	0.065	4.774	-0.9972	78.80
100-120	0.4183	0.0100	4.29	1.3078	0.2354	0.262	0.065	4.774	-0.9972	

[@] Plant available water in the soil layer.

Plant available water in top meter is 227.8 mm.

Definition of the Sevilla Scenarios

Table A20-29. Crop parameters for Sevilla.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m^2 m^{-2})	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	15/03[@]	16/08	15/10[#]	6	31/05	1.0
grass + alfalfa	perennial[$]	31/01[$]	NA	15/04	4	15/04	0.5
		16/04		15/06	4	15/06	0.5
		16/06		15/08	4	15/08	0.5
		16/08		15/10	4	15/10	0.5
potatoes	15/01	31/01	01/05	31/05	4	31/03	0.5
sugar beets	31/10	10/11	12/05	01/07	5	15/04	0.6
winter cereals	15/11	30/11	01/05	31/05	7	28/02	0.40
cabbage		01/03[&]	17/05	01/06	3	01/05	0.5
		15/06[&]	31/08	15/09	3	15/08	0.5
citrus	evergreen	evergreen	NA	NA	6	31/05	1.5
cotton	25/03	05/04	06/06	31/07	5	30/04	0.6
maize	28/02	07/03	01/07	31/07	6	15/06	0.4
strawberries	perennial	30/11[&]	01/08	31/08[*]	3	30/04	0.25
sunflower	01/03	10/03	20/06	15/07	4	15/06	0.60
tomatoes		15/04[&]	01/06	01/07	6	30/05	0.8
vines	perennial	31/03	11/09	30/11	5	15/06	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

Table A20-30. Crop Kc factors for Sevilla.

Crop	Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm)							
	Harvest to Emergence		Emergence to Maximum LAI		Maximum LAI to Senescence		Senescence to Harvest	
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	15/10-14/03	1.00	15/03-30/05	1.05	31/05-15/08	1.10	16/08-15/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	31/05-30/01	1.00	31/01-30/03	1.05	31/03-30/04	1.10	01/05-30/05	0.90
sugar beets	01/07-9/11	1.00	10/11-14/04	1.05	15/04-11/05	1.10	12/05-30/06	0.85
winter cereals	31/05-29/11	1.00	30/11-27/02	1.05	28/02-30/04	1.10	01/05-30/05	0.70
cabbage	15/09-01/03 01/06-14/06	1.00	02/03-30/04 15/06-14/08	1.00	01/05-16/05 15/08-30/08	1.00	17/05-31/05 31/08-14/09	0.93
citrus	NA		NA		All year	0.60	NA	
cotton	31/07-04/04	1.00	05/0429/04	1.08	30/04-05/06	1.15	06/06-30/7	0.90
maize	31/07-06/03	1.00	07/03-14/06	1.05	15/06-6/30	1.10	01/07-30/7	0.83
strawberries	31/08-29/11	1.00	30/11-29/04	1.00	30/04-31/07	1.00	01/08-30/08	1.00
sunflower	15/07-09/03	1.00	10/03-14/06	1.05	15/0619/06	1.10	20/0614/07	0.75
tomatoes	01/07-14/04	1.00	15/04-29/05	1.05	30/05-31/05	1.10	01/06-30/06	0.85
vines	30/11-30/03	1.00	31/03-14/06	0.88	15/06-10/09	0.75	11/09-29/11	0.65

Table A20-31. Soil parameters for Sevilla.

Depth (cm)	Classification	pH-H$_2$O[*]	pH-KCl[†]	Texture (μm)			om (%)	oc (%)	Bulk Density (g cm^{-3})	Depth Factor[@]
				<2	2-50	>50				
0-10	silt loam	7.3	6.6	14	51	35	1.6	0.93	1.21	1.0
10-30	silt loam	7.3	6.6	13	52	35	1.6	0.93	1.23	1.0
30-60	silt loam	7.8	7.1	15	51	34	1.2	0.70	1.25	0.5
60-100	clay loam	8.1	7.4	16	54	30	1.0	0.58	1.27	0.3
100-120	clay loam	8.1	7.4	16	54	30	1.0	0.58	1.27	0.0
120-180	clay loam	8.2	7.5	22	57	21	0.85	0.49	1.27	0.0

[*] Measured at a soil solution ratio of 1:2.5

[†] These values are estimated from the measured water values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

[@] The depth factor indicates the relative transformation rate in the soil layer.

The ground water depth is approximately 2.4 m below the soil surface. If necessary the bottom soil layer can be extended to this depth.

Table A20-32. Soil hydraulic properties for Sevilla, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m^3 m^{-3})	θ_r (m^3 m^{-3})	α (m^{-1})	n	m	Water Content 10kPa (m^3 m^{-3})	Water Content 1600kPa (m^3 m^{-3})	Ksat (m s^{-1}*10^{-6})	λ	AW[@] (mm)
0-10	0.4904	0.0100	2.500	1.2688	0.2119	0.364	0.106	4.819	-1.496	25.8
10-30	0.4836	0.0100	2.450	1.2767	0.2167	0.358	0.101	4.362	-1.374	51.4
30-60	0.4798	0.0100	2.500	1.2695	0.2123	0.356	0.104	4.596	-1.465	75.6
60-100	0.4747	0.0100	2.360	1.2673	0.2109	0.357	0.105	3.911	-1.423	100.8
100-120	0.4747	0.0100	2.360	1.2673	0.2109	0.357	0.105	3.911	-1.423	
120-180	0.4795	0.0100	2.280	1.2297	0.1868	0.377	0.131	3.350	-1.858	

[@] Plant available water in the soil layer.

Plant available water in top meter is 253.6 mm.

Definition of the Thiva Scenarios

Table A20-33. Crop parameters for Thiva.

Crop	Growth Stage Planting (dd/mm)	Growth Stage Emergence (dd/mm)	Growth Stage Senescence (dd/mm)	Growth Stage Harvest (dd/mm)	Max. LAI (m^2 m^{-2})	Max. LAI (dd/mm)	Root Depth (m)
apples	perennial	15/03[@]	21/08	20/10[#]	5	30/06	1.0
grass + alfalfa	perennial	15/04[$]	NA	30/06	4	30/06	0.6
		01/07		15/08	4	15/08	0.6
		16/08		30/09	4	30/09	0.6
		01/10		15/11	4	15/11	0.6
potatoes	15/02	01/03	30/06	30/07	4	30/04	0.6
sugar beets	15/04	01/05	11/08	30/09	5	30/06	0.9
winter cereals	15/11	30/11	31/05	30/06	7.5	30/03	0.8
beans	25/03	01/04	26/05	15/06	4	01/05	0.6
(vegetables)	01/07	08/07	10/09	30/9	4	08/08	0.6
cabbage		15/08[&]	15/11	30/11	4	30/09	0.6
carrots	01/03	15/03	02/05	22/05	4	15/04	0.6
	01/06	15/06	21/08	10/09	4	15/07	0.6
citrus	perennial	evergreen	NA	NA	5		1.0
cotton	01/05	15/05	15/07	30/08	5	15/07	0.8
maize	01/04	20/04	16/08	15/09	4.5	15/06	0.8
onions	15/02	10/04	21/05	30/06	4	15/06	0.6
tobacco		01/05[&]	20/09	30/09	5	15/08	0.6
tomatoes	na	10/04[&]	11/08	10/09	4	30/05	0.6
vines	perennial	15/03	01/08	20/10	4	30/06	1.0

@ leaf emergence

leaf fall

$ "harvest" and "emergence" dates represent the cutting and subsequent regrowth, and so affect above ground biomass but not rooting depth.

& transplanted from seedbed - date indicates day of transplantation.

Table A20-34. Crop Kc factors for Thiva.

Crop	Kc factor as a function of Cropping Periods (expressed in dd/mm-dd/mm)							
	Harvest to Emergence		Emergence to Maximum LAI		Maximum LAI to Senescence		Senescence to Harvest	
	Period	Kc	Period	Kc	Period	Kc	Period	Kc
apples	20/10-14/03	1.00	15/03-29/06	1.05	30/06-20/08	1.10	21/08-19/10	0.98
grass + alfalfa	NA		NA		All year	1.00	NA	
potatoes	30/07-01/03	1.00	02/03-29/04	1.05	30/04-29/06	1.10	30/06-29/07	0.90
sugar beets	30/09-30/04	1.00	01/05-29/06	1.05	30/06-10/08	1.10	11/08-29/09	0.85
winter cereals	30/06-29/11	1.00	30/11-29/03	1.05	30/03-30/05	1.10	31/05-29/06	0.70
beans (vegetables)	30/9-31/03 15/06-07/07	1.00	01/04-4/30 08/07-07/08	1.05	01/05-25/05 08/08-09/09	1.10	26/05-14/06 10/09-29/09	0.70
cabbage	30/11-14/08	1.00	15/08-29/09	1.00	30/09-14/11	1.00	15/11-29/11	0.93
carrots	10/09-14/03 22/05-14/06	1.00	15/03-14/04 15/06-14/07	1.03	15/04-01/05 15/07-20/08	1.05	02/05-21/05 21/08-09/09	0.90
citrus	NA		NA		All year	0.60	NA	
cotton	30/08-14/05	1.00	15/05-14/07	1.08			15/07-29/08	0.90
maize	15/09-19/04	1.00	20/04-14/06	1.05	15/06-15/08	1.10	16/08-14/09	0.83
onions	30/06-09/04	1.00	10/04-14/06	0.98	15/06-20/05	0.95	21/05-29/06	0.85
tobacco	30/09-30/04	1.00	01/05-14/08	1.00	15/08-19/09	1.00	20/09-29/09	0.93
tomatoes	10/09-09/04	1.00	10/04-29/05	1.05	30/05-10/08	1.10	11/08-09/09	0.85
vines	20/10-14/03	1.00	15/03-29/06	0.88	30/06-31/07	0.75	01/08-19/10	0.65

Table A20-35. Soil parameters for Thiva.

Horizon	Depth (cm)	Classification	pH-H_2O*	pH-KCl[†]	Texture (µm)			om (%)	oc (%)	Bulk Density (g cm^{-3})	Depth Factor[@]
					<2	2-50	>50				
Ap1	0-30	loam	7.7	7.0	25.3	42.8	31.9	1.28	0.74	1.42	1.0
Ap2	30-45	loam	7.7	7.0	25.3	42.8	31.9	1.28	0.74	1.42	0.5
Bw	45-60	clay loam	7.8	7.1	29.6	38.7	31.7	0.98	0.57	1.43	0.5
Bw	60-85	clay loam	7.8	7.1	31.9	35.7	32.3	0.53	0.31	1.48	0.3
Ck1	85-100	clay loam	7.8	7.1	32.9	35.6	31.5	0.31	0.18	1.56	0.3
Ck1	100-???	clay loam	7.8	7.1	32.9	35.6	31.5	0.31	0.18	1.56	0.0

[†] These values are estimated from the measured KCl values by assuming a standard difference of 0.7 pH units (Barrere et al, 1988)

* Measured at a soil solution ratio of 1:2.5

[@] The depth factor indicates the relative transformation rate in the soil layer.

Depth of ground water > 5 m.

Table A20-36. Soil hydraulic properties for Thiva, Van Genuchten/Mualem parameters.

Depth (cm)	θ_s (m^3 m^{-3})	θ_r (m^3 m^{-3})	α (m^{-1})	n	m	Water Content 10kPa (m^3 m^{-3})	Water Content 1600kPa (m^3 m^{-3})	Ksat (m s^{-1}*10^{-6})	λ	AW[@] (mm)
0-30	0.4341	0.01	3.33	1.1804	0.15283	0.340	0.147	3.48	-3.162	58.02
30-45	0.4341	0.01	3.33	1.1804	0.15283	0.340	0.147	3.48	-3.162	29.01
45-60	0.4412	0.01	3.58	1.1330	0.117387	0.365	0.196	2.28	-3.402	25.43
60-85	0.4279	0.01	3.62	1.1252	0.111269	0.357	0.199	1.83	-3.312	39.70
85-100	0.4041	0.01	3.37	1.1145	0.102737	0.345	0.202	1.26	-3.259	21.44
100-???	0.4041	0.01	3.37	1.1145	0.102737	0.345	0.202	1.26	-3.259	

[@] Plant available water in the soil layer.

Plant available water in top meter of soil is 142.9 mm.

Layer 100 - ??? cm copied from layer 85 - 100 cm; this layer can be extended according to the needs of the models.

Latitude and longitude of the FOCUS Scenario Locations

Table A20-37. Latitude and longitude of the FOCUS scenario locations.

Location	Latitude	Longitude
Châteaudun	47° 98' N	1° 75' E
Hamburg	53° 63' N	10° 00' E
Jokioinen	60° 82' N	23° 50' E
Kremsmünster	48° 05' N	14° 13' E
Okehampton	50° 80' N	3° 80' W
Piacenza	44° 92' N	9° 73' E
Porto	41° 23' N	8° 68' W
Sevilla	37° 42' N	5° 88' W
Thiva	37° 97' N	23° 72' E

References

Barrere, C., Bastide, J., Coste, C.M. 1988. Relations entre la vitesse de degradation du propyzamide et les proprietes physicochimique des sols. Weed research 28:93-99.

APPENDIX 21. CALIBRATION OF EVAPOTRANSPIRATION AT PIACENZA, SEVILLA, AND THIVA

PELMO runs were made with a range of ANETD parameters and the resulting average annual evapotranspiration over the 20 year simulation period was compared with that obtained from PEARL runs. For this set of comparisons, runoff was switched off in PELMO.

Piacenza

Comparisons performed for tobacco and winter wheat (Table A21-1) show that the evapotranspiration is not very sensitive to the ANETD at values greater than 5 cm. The values providing the best fit were 15 and 20 cm, although the deviations with the value of 25 cm used by FOCUS (2000) are less than 20 mm. A value of 15 cm was chosen since tobacco is more representative of the timing of the majority of the crops.

Table A21-1. Annual average evapotranspiration in Piacenza (mm)

Piacenza	Tobacco	Winter Wheat
PEARL	**702**	**574**
PELMO (ANETD=0 cm)	516	-
PELMO (ANETD=5 cm)	658	-
PELMO (ANETD=10 cm)	687	539
PELMO (ANETD=15 cm)	**702**	559
PELMO (ANETD=20 cm)	712	**571**
PELMO (ANETD=25 cm)*	721	580

* FOCUS (2000)

Sevilla

Comparisons performed for sunflowers and winter wheat (Table A21-2) show quite different results. An ANETD value of 15 cm provides a good fit with PEARL for sunflowers. None of the ANETD values provide a good fit with PEARL for winter wheat, probably because of upwards flow from ground water during the hot non-irrigated summer. A value of 15 cm was chosen since sunflowers are more representative of the timing of the majority of the crops. The use of 15 cm results in a significant drop in evapotranspiration compared to the value of 30 cm used by FOCUS (2000).

Table A21-2. Annual average evapotranspiration in Sevilla (mm).

Sevilla	Sunflowers	Winter Wheat
PEARL	**869**	**538**
PELMO (ANETD=0 cm)	610	-
PELMO (ANETD= 5 cm)	776	-
PELMO (ANETD=10 cm)	831	-
PELMO (ANETD=15 cm)	**867**	372
PELMO (ANETD=20 cm)	892	375
PELMO (ANETD=25 cm)	910	378
PELMO (ANETD=30 cm)*	924	**379**

* FOCUS (2000)

Thiva

Comparisons performed for cabbage and winter wheat (Table A21-3) show quite different results. An ANETD value of 20 cm provides a good fit with PEARL for cabbage. Similar to Sevilla, none of the ANETD values provide a good fit with PEARL for winter wheat, probably because of upwards flow from ground water during the hot non-irrigated summer. A value of 20 cm was chosen for since sunflowers are more representative of the timing of the majority of the crops. The use of 20 cm results in a significant drop in evapotranspiration compared to the value of 30 cm used by FOCUS (2000).

Table 2: Annual average soil evapotranspiration in Thiva (mm).

Thiva	Cabbage	Winter Wheat
PEARL	**707**	**435**
PELMO (ANETD=10 cm)	552	-
PELMO (ANETD=15 cm)	652	334
PELMO (ANETD=20 cm)	**711**	339
PELMO (ANETD=30 cm)*	746	**340**
PELMO (ANETD=35 cm)	767	-

* FOCUS (2000)

References

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APPENDIX 22. IRRIGATION DATA

As part of the process for revising the irrigation amounts in the Tier I scenarios, the work group collected irrigation data relevant to the five irrigated locations. These data are presented here.

Châteaudun

Table A22-1. Irrigation data for Châteaudun.

Crop	Average Annual FOCUS 2000 Irrigation (mm)	Measured (M) or Estimated (E) irrigation (mm)	Source
Maize	332	Approximately 2x too high median value 160mm for Beauce region	Local expert region Beauce (Golas(2004))
Sugar Beet	359	~80	Institute Technique de la Betterave 1994

Piacenza

Table A22-2. Irrigation data for Piacenza.

Crop	Average Annual FOCUS (2000) Irrigation (mm)	Measured (M) or Estimated (E) irrigation (mm)	Source
Maize	367	230(E)	ARPA (2004)
		180 – 250 (E) 1996	SUSAP model
		124 (M)	Miao *et al.* (2004)
Potatoes/Tomatoes	382/328	232 (E)	ARPA (2004) for vegetables
Apples	361	238	ARPA (2004) orchard/fruit trees

Porto

Estimated irrigation amounts for Porto (Beira Litoral region) are available from IDRHA.

Sevilla

Table A22-3. Irrigation data for Sevilla.

Crop	Average FOCUS (2000) Irrigation (mm)	Measured (M) or Estimated (E) irrigation (mm)	Source
Maize	603	564(M) in 1992 562 (M) in 1993	Fernandez *et al.* (1996)
		448 (M) in 1996 501 (M) in 1997 713 (M) in 1998 545 (M) in 1999	Lorite *et al.* (2004b)
		500 (E)	IDRHA (Algarve)
Sugar Beet	463	297 (M) in 1996 399 (M) in 1997 709 (M) in 1998 421 (M) in 1999	Lorite *et al.* (2004b)
Potatoes	270	280(E)	IDRHA (Algarve)
Tomatoes	501	440(E)	IDRHA (Algarve)

Thiva

Table A22-4. irrigation data collected for Thiva.

Crop	Average FOCUS Irrigation (Sevilla) (mm)	Measured (M) or Estimated (E) irrigation (mm)	Source
Potatoes	564	490 autumn 460 spring	Ministerial decision
Cotton	?	510	Ministerial decision
Apples	661	570	Ministerial decision
Maize	602	520	Ministerial decision
Tobacco		480	Ministerial decision
Grapes		580	Ministerial decision
Citrus		510	Ministerial decision

These data are taken from a Ministerial Decision from 1989 (F16/6631from 2/6/1989) concerning the determination of the needs of different crops and calculation of appropriate irrigation water.

References

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APPENDIX 23. RESULTS OF SIMULATIONS COMPARING THE CURRENT AND THE PROPOSED SCENARIOS

Table A23-1. PECgw for Pesticide D at 1 m.

Location	Crop	PECgw (µg/L) for Pesticide D at 1 m							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Châteaudun	apples	0.3618	0.3580	0.1971	-	0.5763	0.3870	0.3199	-
Châteaudun	cabbage	0.1598	0.1182	0.0662	-	0.2855	0.0084	0.0039	-
Châteaudun	carrots	0.1843	0.1027	0.0450	-	0.2664	0.0060	0.0024	-
Châteaudun	cereals (spring)	0.0060	0.0021	0.0012	-	0.0092	0.0002	0.0000	-
Châteaudun	cereals (winter)	0.0921	0.0302	0.0236	-	0.1618	0.0132	0.0156	-
Châteaudun	grass	0.0906	0.0678	0.0255	-	0.0962	0.0067	0.0019	-
Châteaudun	maize	0.0751	0.0280	0.0233	-	0.1911	0.0012	0.0007	-
Châteaudun	onions	0.0163	0.0143	0.0079	-	0.1888	0.0078	0.0030	-
Châteaudun	peas	0.0024	0.0013	0.0009	-	0.0033	0.0000	0.0000	-
Châteaudun	potatoes	0.0622	0.0369	0.0247	-	0.2258	0.0014	0.0007	-
Châteaudun	rape (winter)	0.0833	0.0424	0.0471	-	0.1102	0.0270	0.0318	-
Châteaudun	sugar beets	0.4275	0.1436	0.0586	-	0.3393	0.0393	0.0131	-
Châteaudun	tomatoes	0.0848	0.0363	0.0200	-	0.3141	0.0101	0.0052	-
Châteaudun	vines	0.2532	0.2473	0.1349	-	0.6473	0.4510	0.4294	-
Hamburg	apples	0.3488	0.2486	0.1522	-	1.9109	0.1210	0.1383	-
Hamburg	beans (field)	0.1786	0.1022	0.0966	-	0.2358	0.0462	0.0493	-
Hamburg	cabbage	0.7519	0.5922	0.4861	-	0.7704	0.2430	0.2053	-
Hamburg	carrot	0.6296	0.4643	0.3616	-	0.6890	0.2310	0.2248	-
Hamburg	cereals (spring)	0.2025	0.1162	0.1190	-	0.2632	0.0467	0.0528	-
Hamburg	cereals (winter)	1.8052	1.8610	1.5940	-	1.2972	1.0600	1.2260	-
Hamburg	grass	0.1915	0.1018	0.0927	-	0.2010	0.0261	0.0871	-
Hamburg	maize	0.2209	0.1531	0.1355	-	0.2939	0.0731	0.0690	-
Hamburg	onions	0.1735	0.1038	0.0842	-	0.1941	0.0505	0.0425	-
Hamburg	peas	0.1763	0.1049	0.0913	-	0.2258	0.0446	0.0385	-
Hamburg	potato	0.1665	0.1378	0.1234	-	0.1980	0.0518	0.0351	-
Hamburg	rape (winter)	1.0476	0.8316	0.8686	-	0.8392	0.5220	0.6456	-
Hamburg	strawberries	0.6198	0.2516	0.1262	-	0.6833	0.0813	0.1140	-
Hamburg	sugar beets	0.1716	0.1104	0.0793	-	0.2405	0.0630	0.0635	-
Hamburg	vines	0.2553	0.3188	0.2075	-	0.2927	0.1470	0.1670	-
Jokioinen	apples	0.0490	0.0678	0.0602	-	0.0492	0.1410	0.0042	-
Jokioinen	bush berries	0.0824	0.0504	0.0457	-	0.0693	0.0060	0.0017	-
Jokioinen	cabbage	0.0239	0.0326	0.0327	-	0.0233	0.0008	0.0001	-
Jokioinen	carrots	0.0231	0.0362	0.0426	-	0.0274	0.0007	0.0001	-
Jokioinen	cereals (spring)	0.0317	0.0375	0.0392	-	0.0258	0.0010	0.0001	-
Jokioinen	cereals (winter)	0.3272	0.4230	0.3431	-	0.2091	0.0758	0.0053	-
Jokioinen	grass	0.0420	0.0492	0.0411	-	0.0414	0.1600	0.0023	-
Jokioinen	onions	0.0190	0.0239	0.0391	-	0.0176	0.0003	0.0001	-
Jokioinen	peas	0.0343	0.0409	0.0479	-	0.0288	0.0007	0.0001	-
Jokioinen	potatoes	0.0261	0.0343	0.0414	-	0.0283	0.0003	0.0000	-
Jokioinen	rape (summer)	0.0273	0.0369	0.0405	-	0.0262	0.0011	0.0001	-

Table A23-1 (continued). PECgw for Pesticide D at 1 m.

Location	Crop	PECgw (µg/L) for Pesticide D at 1 m							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Jokioinen	strawberries	0.0343	0.0305	0.0426	-	0.0338	0.0014	0.0005	-
Jokioinen	sugar beets	0.0387	0.0435	0.0380	-	0.0342	0.0017	0.0001	-
Kremsmünster	apples	0.2382	0.3012	0.1195	-	0.3578	0.1420	0.1024	-
Kremsmünster	beans (field)	0.1395	0.1213	0.0596	-	0.2000	0.0078	0.0016	-
Kremsmünster	cabbage	0.3612	0.4019	0.2434	-	0.3791	0.0365	0.0096	-
Kremsmünster	carrots	0.3947	0.4653	0.2459	-	0.4663	0.0334	0.0084	-
Kremsmünster	cereals (spring)	0.1654	0.1505	0.0678	-	0.1919	0.0147	0.0040	-
Kremsmünster	cereals (winter)	0.5745	0.5397	0.4074	-	0.5478	0.1470	0.0661	-
Kremsmünster	grass	0.1111	0.1166	0.0385	-	0.1208	0.0576	0.0144	-
Kremsmünster	maize	0.1402	0.1481	0.0959	-	0.1908	0.0052	0.0017	-
Kremsmünster	onions	0.1102	0.1063	0.0549	-	0.1440	0.0086	0.0019	-
Kremsmünster	potatoes	0.1004	0.1056	0.0557	-	0.1281	0.0026	0.0004	-
Kremsmünster	rape (winter)	0.5842	0.5617	0.4921	-	0.5014	0.2720	0.2376	-
Kremsmünster	strawberries	0.2446	0.1551	0.0518	-	0.2978	0.0173	0.0074	-
Kremsmünster	sugar beets	0.1058	0.1181	0.0430	-	0.1743	0.0283	0.0058	-
Kremsmünster	vines	0.1965	0.4361	0.1909	-	0.2512	0.2370	0.2022	-
Okehampton	apples	0.3338	0.5915	0.3718	-	0.4485	0.9870	0.3248	-
Okehampton	beans (field)	0.2151	0.2749	0.2413	-	0.3174	0.0310	0.0337	-
Okehampton	cereals (spring)	0.2936	0.2907	0.2020	-	0.3328	0.0346	0.0377	-
Okehampton	cereals (winter)	1.6406	1.8038	1.7650	-	1.9732	1.0900	1.7070	-
Okehampton	grass	0.2530	0.3662	0.2266	-	0.2515	1.1100	0.0984	-
Okehampton	linseed	0.2190	0.2859	0.2365	-	0.2531	0.0537	0.0597	-
Okehampton	maize	0.4298	0.4214	0.3694	-	0.4623	0.0189	0.0196	-
Okehampton	peas	0.2007	0.2063	0.1781	-	0.2332	0.0134	0.0153	-
Okehampton	potatoes	0.2332	0.2634	0.2381	-	0.2997	0.0094	0.0096	-
Okehampton	rape (summer)	0.2571	0.2939	0.2290	-	0.2745	0.0597	0.0375	-
Okehampton	rape (winter)	0.7564	0.8906	0.9572	-	0.8349	0.4090	0.6886	-
Okehampton	sugar beets	0.2151	0.3161	0.2509	-	0.2667	0.0496	0.0609	-
Piacenza	apples	0.2173	0.7635	0.3270	-	1.3552	2.2600	0.3663	-
Piacenza	cereals (winter)	0.7159	1.0247	0.7932	-	1.6928	2.0800	1.4320	-
Piacenza	citrus	0.2886	0.4138	0.2622	-	1.6609	4.2400	0.6345	-
Piacenza	grass	0.2293	0.5785	0.1091	-	0.7350	1.4800	0.1024	-
Piacenza	maize	0.2022	0.3117	0.1160	-	0.7182	0.3910	0.1347	-
Piacenza	potatoes	0.1383	0.2145	0.0747	-	0.7016	0.2330	0.0531	-
Piacenza	rape (winter)	1.1720	1.8819	2.0180	-	5.5158	4.2100	5.1590	-
Piacenza	soybeans	0.1527	0.1543	0.0531	-	0.4719	0.1590	0.0522	-
Piacenza	sugar beets	0.2202	0.3613	0.0994	-	1.0647	0.3440	0.0863	-
Piacenza	sunflowers	0.1650	0.4885	0.1641	-	0.9875	0.4190	0.1262	-
Piacenza	tobacco	0.1705	0.3219	0.1326	-	0.7428	0.3740	0.1318	-
Piacenza	tomatoes	0.1844	0.3805	0.1069	-	1.1246	0.4650	0.1145	-
Piacenza	vines	0.2371	0.5985	0.2025	-	1.3510	2.8800	0.4505	-
Porto	apples	0.0550	0.1663	0.0525	-	0.0000	0.0085	0.0000	-
Porto	beans (veg)	0.0365	0.0774	0.0378	-	0.0000	0.0000	0.0000	-

568

Table A23-1 (continued). PECgw for Pesticide D at 1 m.

Location	Crop	PECgw (µg/L) for Pesticide D at 1 m							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Porto	cabbage	0.3323	0.7211	0.2603	-	0.0010	0.0000	0.0000	-
Porto	carrots	0.2080	0.4630	0.1716	-	0.3507	0.0000	0.0000	-
Porto	cereals (spring)	0.0351	0.1628	0.0549	-	0.0000	0.0000	0.0000	-
Porto	cereals (winter)	1.2923	2.5956	2.0680	-	0.0087	0.0013	0.0006	-
Porto	citrus	0.0466	0.0908	0.0462	-	0.0000	0.0104	0.0000	-
Porto	grass	0.0441	0.1009	0.0203	-	0.0000	0.0038	0.0000	-
Porto	maize	0.0229	0.0313	0.0125	-	0.0000	0.0000	0.0000	-
Porto	onions	0.0376	0.0937	0.0284	-	0.0000	0.0000	0.0000	-
Porto	potatoes	0.0315	0.1179	0.0408	-	0.0000	0.0000	0.0000	-
Porto	rape (summer)	0.0592	0.2092	0.1024	-	0.0000	0.0000	0.0000	-
Porto	rape (winter)	0.7993	1.9727	1.2380	-	0.0040	0.0007	0.0002	-
Porto	sugar beets	0.0856	0.3522	0.1248	-	0.0000	0.0000	0.0000	-
Porto	tomatoes	0.0367	0.0672	0.0407	-	0.0000	0.0000	0.0000	-
Porto	vines	0.0322	0.1185	0.0500	-	0.0000	0.0086	0.0000	-
Sevilla	apples	0.3553	0.1040	0.0397	-	0.3059	0.0036	0.0011	-
Sevilla	cabbage	0.0656	0.0026	0.0012	-	0.3507	0.0000	0.0000	-
Sevilla	cereals (winter)	0.0000	0.0136	0.0347	-	0.1107	0.0001	0.0000	-
Sevilla	citrus	0.0980	0.0281	0.0105	-	0.4434	0.1500	0.0181	-
Sevilla	cotton	0.0098	0.0046	0.0031	-	0.0611	0.0000	0.0000	-
Sevilla	grass	0.0082	0.0041	0.0008	-	0.0190	0.0010	0.0000	-
Sevilla	maize	0.0005	0.0003	0.0003	-	0.0067	0.0000	0.0000	-
Sevilla	potatoes	0.0015	0.0015	0.0009	-	0.0155	0.0000	0.0000	-
Sevilla	strawberries	0.0176	0.0903	0.1007	-	0.1278	0.0000	0.0000	-
Sevilla	sugar beets	0.0932	0.0941	0.1122	-	0.3054	0.0014	0.0007	-
Sevilla	sunflowers	0.0018	0.0007	0.0006	-	0.0421	0.0000	0.0000	-
Sevilla	tomatoes	0.0026	0.0013	0.0014	-	0.0885	0.0000	0.0000	-
Sevilla	vines	0.1324	0.0433	0.0172	-	0.2943	0.0134	0.0026	-
Thiva	apples	0.2425	0.0807	0.0200	-	0.2368	0.0487	0.0020	-
Thiva	beans (veg)	0.0666	0.0274	0.0080	-	0.1266	0.0000	0.0000	-
Thiva	cabbage	0.0620	0.0579	0.0169	-	0.0488	0.0008	0.0001	-
Thiva	carrots	0.0303	0.0095	0.0021	-	0.1161	0.0000	0.0000	-
Thiva	cereals (winter)	0.0331	0.0403	0.0204	-	0.1592	0.0174	0.0040	-
Thiva	citrus	0.0301	0.0461	0.0099	-	0.4053	0.4830	0.0432	-
Thiva	cotton	0.0024	0.0030	0.0009	-	0.1128	0.0000	0.0000	-
Thiva	grass	0.0239	0.0235	0.0018	-	0.0184	0.0393	0.0000	-
Thiva	maize	0.0159	0.0105	0.0042	-	0.1142	0.0000	0.0000	-
Thiva	onions	0.0003	0.0009	0.0001	-	0.0673	0.0000	0.0000	-
Thiva	potatoes	0.0067	0.0036	0.0012	-	0.0348	0.0000	0.0000	-
Thiva	sugar beets	0.0204	0.0111	0.0020	-	0.1252	0.0001	0.0000	-
Thiva	tobacco	0.0029	0.0011	0.0004	-	0.0225	0.0000	0.0000	-
Thiva	tomatoes	0.0069	0.0033	0.0012	-	0.0385	0.0000	0.0000	-
Thiva	vines	0.0361	0.0253	0.0071	-	0.2601	0.2240	0.0260	-

Table A23-2. Annual averages of rainfall and irrigation.

Location	Crop	Rainfall (mm) FOCUS 2000 and 2009 All Models	Irrigation (mm) FOCUS 2009 PEARL	Irrigation (mm) FOCUS 2009 PELMO and PRZM	Irrigation (mm) FOCUS 2009 MACRO	Irrigation (mm) FOCUS 2000 All Models
Châteaudun	apples	648	350	369	-	323
Châteaudun	cabbage	648	185	198	-	284
Châteaudun	carrots	648	175	171	-	284
Châteaudun	cereals (spring)	648	0	0	-	0
Châteaudun	cereals (winter)	648	0	0	-	0
Châteaudun	grass	648	338	331	-	303
Châteaudun	maize	648	264	255	-	323
Châteaudun	onions	648	112	139	-	284
Châteaudun	peas	648	0	0	-	0
Châteaudun	potatoes	648	200	211	-	311
Châteaudun	rape (winter)	648	0	0	-	0
Châteaudun	sugar beets	648	395	328	-	349
Châteaudun	tomatoes	648	176	177	-	284
Châteaudun	vines	648	243	237	-	323
Hamburg	all crops	786	0	0	-	0
Jokioinen	all crops	650	0	0	-	0
Kremsmünster	all crops	899	0	0	-	0
Okehampton	all crops	1038	0	0	-	0
Piacenza	apples	857	156	448	-	361
Piacenza	cereals (winter)	857	0	0	-	0
Piacenza	citrus	857	63	241	-	361
Piacenza	grass	857	217	457	-	369
Piacenza	maize	857	188	399	-	365
Piacenza	potatoes	857	221	335	-	381
Piacenza	rape (winter)	857	0	0	-	0
Piacenza	soybeans	857	218	341	-	365
Piacenza	sugar beets	857	168	294	-	392
Piacenza	sunflowers	857	176	403	-	365
Piacenza	tobacco	857	159	358	-	365
Piacenza	tomatoes	857	107	234	-	328
Piacenza	vines	857	97	290	-	361
Porto	apples	1150	398	509	-	0

Table A23-2 (continued). Annual averages of rainfall and irrigation.

Location	Crop	Rainfall (mm)	Irrigation (mm)			
		FOCUS 2000 and 2009	FOCUS 2009			FOCUS 2000
		All Models	PEARL	PELMO and PRZM	MACRO	All Models
Porto	beans (veg)	1150	315	415	-	0
Porto	cabbage	1150	290	399	-	0
Porto	carrots	1150	212	299	-	0
Porto	cereals (spring)	1150	0	0	-	0
Porto	cereals (winter)	1150	0	0	-	0
Porto	citrus	1150	194	309	-	0
Porto	grass	1150	376	541	-	0
Porto	maize	1150	310	393	-	0
Porto	onions	1150	8	93	-	0
Porto	potatoes	1150	79	138	-	0
Porto	rape (summer)	1150	176	312	-	0
Porto	rape (winter)	1150	0	0	-	0
Porto	sugar beets	1150	71	177	-	0
Porto	tomatoes	1150	267	361	-	0
Porto	vines	1150	255	310	-	0
Sevilla	apples	493	1088	916	-	829
Sevilla	cabbage	493	538	623	-	504
Sevilla	cereals (winter)	493	0	0	-	0
Sevilla	citrus	493	815	729	-	829
Sevilla	cotton	493	242	275	-	605
Sevilla	grass	493	1027	1171	-	871
Sevilla	maize	493	380	430	-	605
Sevilla	potatoes	493	178	205	-	265
Sevilla	strawberries	493	546	913	-	504
Sevilla	sugar beets	493	302	298	-	461
Sevilla	sunflowers	493	316	361	-	605
Sevilla	tomatoes	493	162	181	-	504
Sevilla	vines	493	855	757	-	829
Thiva	apples	500	747	744	-	660
Thiva	beans (veg)	500	471	515	-	525
Thiva	cabbage	500	185	214	-	525
Thiva	carrots	500	433	491	-	525

Table A23-2 (continued). Annual averages of rainfall and irrigation.

Location	Crop	Rainfall (mm) FOCUS 2000 and 2009	Irrigation (mm) FOCUS 2009			FOCUS 2000
		All Models	PEARL	PELMO and PRZM	MACRO	All Models
Thiva	cereals (winter)	500	0	0	-	0
Thiva	citrus	500	434	533	-	660
Thiva	cotton	500	260	312	-	604
Thiva	grass	500	728	856	-	613
Thiva	maize	500	505	599	-	604
Thiva	onions	500	58	217	-	525
Thiva	potatoes	500	356	393	-	567
Thiva	sugar beets	500	463	516	-	667
Thiva	tobacco	500	553	615	-	604
Thiva	tomatoes	500	526	578	-	525
Thiva	vines	500	514	483	-	660

Table A23-3. Annual averages of runoff.

Location	Crop	Runoff (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Châteaudun	apples	0	0	0	-	0	12	11	-
Châteaudun	cabbage	0	0	0	-	0	84	75	-
Châteaudun	carrots	0	0	0	-	0	106	97	-
Châteaudun	cereals (spring)	0	0	0	-	0	44	46	-
Châteaudun	cereals (winter)	0	0	0	-	0	31	30	-
Châteaudun	grass	0	0	0	-	0	6	5	-
Châteaudun	maize	0	0	0	-	0	149	137	-
Châteaudun	onions	0	0	0	-	0	77	69	-
Châteaudun	peas	0	0	0	-	0	50	50	-
Châteaudun	potatoes	0	0	0	-	0	144	131	-
Châteaudun	rape (winter)	0	0	0	-	0	21	20	-
Châteaudun	sugar beets	0	0	0	-	0	77	71	-
Châteaudun	tomatoes	0	0	0	-	0	82	74	-
Châteaudun	vines	0	0	0	-	0	12	11	-
Hamburg	apples	0	0	0	-	0	3	3	-
Hamburg	beans (field)	0	0	0	-	0	53	55	-
Hamburg	cabbage	0	0	0	-	0	41	45	-
Hamburg	carrot	0	0	0	-	0	43	46	-
Hamburg	cereals (spring)	0	0	0	-	0	47	50	-
Hamburg	cereals (winter)	0	0	0	-	0	25	24	-
Hamburg	grass	0	0	0	-	0	2	3	-
Hamburg	maize	0	0	0	-	0	58	61	-
Hamburg	onions	0	0	0	-	0	47	50	-
Hamburg	peas	0	0	0	-	0	51	54	-
Hamburg	potato	0	0	0	-	0	58	59	-
Hamburg	rape (winter)	0	0	0	-	0	16	15	-
Hamburg	strawberries	0	0	0	-	0	10	12	-
Hamburg	sugar beets	0	0	0	-	0	41	44	-
Hamburg	vines	0	0	0	-	0	4	5	-
Jokioinen	apples	0	0	0	-	0	23	20	-
Jokioinen	bush berries	0	0	0	-	0	20	19	-
Jokioinen	cabbage	0	0	0	-	0	88	92	-
Jokioinen	carrots	0	0	0	-	0	89	90	-
Jokioinen	cereals (spring)	0	0	0	-	0	96	100	-
Jokioinen	cereals (winter)	0	0	0	-	0	52	54	-
Jokioinen	grass	0	0	0	-	0	18	18	-
Jokioinen	onions	0	0	0	-	0	98	102	-
Jokioinen	peas	0	0	0	-	0	103	108	-
Jokioinen	potatoes	0	0	0	-	0	114	114	-
Jokioinen	rape (summer)	0	0	0	-	0	94	98	-
Jokioinen	strawberries	0	0	0	-	0	39	40	-
Jokioinen	sugar beets	0	0	0	-	0	84	87	-
Kremsmünster	apples	4	0	0	-	6	30	28	-

Table A23-3 (continued). Annual averages of runoff.

Location	Crop	Runoff (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Kremsmünster	beans (field)	4	0	0	-	5	145	141	-
Kremsmünster	cabbage	4	0	0	-	3	112	112	-
Kremsmünster	carrots	4	0	0	-	3	124	122	-
Kremsmünster	cereals (spring)	4	0	0	-	3	121	120	-
Kremsmünster	cereals (winter)	4	0	0	-	5	100	94	-
Kremsmünster	grass	3	0	0	-	1	20	19	-
Kremsmünster	maize	5	0	0	-	4	174	171	-
Kremsmünster	onions	4	0	0	-	5	123	121	-
Kremsmünster	potatoes	4	0	0	-	3	170	165	-
Kremsmünster	rape (winter)	4	0	0	-	6	87	81	-
Kremsmünster	strawberries	4	0	0	-	1	63	60	-
Kremsmünster	sugar beets	4	0	0	-	3	108	109	-
Kremsmünster	vines	8	0	0	-	13	31	30	-
Okehampton	apples	0	0	0	-	0	23	24	-
Okehampton	beans (field)	0	0	0	-	0	153	152	-
Okehampton	cereals (spring)	0	0	0	-	0	151	149	-
Okehampton	cereals (winter)	0	0	0	-	0	89	86	-
Okehampton	grass	0	0	0	-	0	17	17	-
Okehampton	linseed	0	0	0	-	0	136	135	-
Okehampton	maize	1	0	0	-	0	193	188	-
Okehampton	peas	0	0	0	-	0	165	164	-
Okehampton	potatoes	0	0	0	-	0	190	187	-
Okehampton	rape (summer)	0	0	0	-	0	151	148	-
Okehampton	rape (winter)	0	0	0	-	0	68	66	-
Okehampton	sugar beets	0	0	0	-	0	132	130	-
Piacenza	apples	0	0	0	-	0	2	2	-
Piacenza	cereals (winter)	0	0	0	-	0	52	52	-
Piacenza	citrus	0	0	0	-	0	2	2	-
Piacenza	grass	0	0	0	-	0	1	0	-
Piacenza	maize	0	0	0	-	0	71	61	-
Piacenza	potatoes	0	0	0	-	0	80	69	-
Piacenza	rape (winter)	0	0	0	-	0	36	35	-
Piacenza	soybeans	0	0	0	-	0	90	75	-
Piacenza	sugar beets	0	0	0	-	0	67	60	-
Piacenza	sunflowers	0	0	0	-	0	85	75	-
Piacenza	tobacco	0	0	0	-	0	95	81	-
Piacenza	tomatoes	0	0	0	-	0	89	79	-
Piacenza	vines	0	0	0	-	0	7	6	-
Porto	apples	30	0	0	-	31	48	49	-
Porto	beans (veg)	24	0	0	-	44	281	286	-
Porto	cabbage	31	0	0	-	44	215	216	-
Porto	carrots	30	0	0	-	48	249	250	-
Porto	cereals (spring)	20	0	0	-	46	271	276	-

Table A23-3 (continued). Annual averages of runoff.

Location	Crop	Runoff (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Porto	cereals (winter)	25	0	0	-	55	173	177	-
Porto	citrus	48	0	0	-	43	50	51	-
Porto	grass	32	0	0	-	37	39	41	-
Porto	maize	25	0	0	-	39	306	308	-
Porto	onions	29	0	0	-	57	275	277	-
Porto	potatoes	30	0	0	-	54	303	307	-
Porto	rape (summer)	20	0	0	-	38	273	278	-
Porto	rape (winter)	23	0	0	-	54	109	111	-
Porto	sugar beets	19	0	0	-	39	275	280	-
Porto	tomatoes	20	0	0	-	42	272	276	-
Porto	vines	33	0	0	-	36	49	50	-
Sevilla	apples	0	0	0	-	0	173	132	-
Sevilla	cabbage	0	0	0	-	0	262	218	-
Sevilla	cereals (winter)	0	0	0	-	0	101	96	-
Sevilla	citrus	0	0	0	-	0	193	166	-
Sevilla	cotton	0	0	0	-	0	354	283	-
Sevilla	grass	0	0	0	-	0	106	59	-
Sevilla	maize	0	0	0	-	0	391	320	-
Sevilla	potatoes	0	0	0	-	0	236	209	-
Sevilla	strawberries	0	0	0	-	0	164	123	-
Sevilla	sugar beets	0	0	0	-	0	196	157	-
Sevilla	sunflowers	0	0	0	-	0	420	349	-
Sevilla	tomatoes	0	0	0	-	0	300	252	-
Sevilla	vines	0	0	0	-	0	178	145	-
Thiva	apples	2	0	0	-	0	69	49	-
Thiva	beans (veg)	1	0	0	-	0	275	281	-
Thiva	cabbage	2	0	0	-	0	287	269	-
Thiva	carrots	1	0	0	-	0	228	195	-
Thiva	cereals (winter)	0	0	0	-	0	66	69	-
Thiva	citrus	2	0	0	-	0	78	66	-
Thiva	cotton	0	0	0	-	0	279	241	-
Thiva	grass	2	0	0	-	0	40	23	-
Thiva	maize	1	0	0	-	0	342	307	-
Thiva	onions	1	0	0	-	0	281	249	-
Thiva	potatoes	1	0	0	-	0	311	278	-
Thiva	sugar beets	1	0	0	-	0	251	210	-
Thiva	tobacco	1	0	0	-	0	253	221	-
Thiva	tomatoes	1	0	0	-	0	215	176	-
Thiva	vines	2	0	0	-	0	75	64	-

Table A23-4. Annual Averages of potential evapotranspiration (not reported by PRZM).

Location	Crop	Potential Evapotranspiration (mm)					
		FOCUS 2009			FOCUS 2000		
		PEARL	PELMO	MACRO	PEARL	PELMO	MACRO
Châteaudun	apples	817	817	-	730	733	-
Châteaudun	cabbage	765	765	-	692	719	-
Châteaudun	carrots	766	765	-	687	711	-
Châteaudun	cereals (spring)	770	768	-	680	682	-
Châteaudun	cereals (winter)	767	767	-	675	622	-
Châteaudun	grass	774	774	-	741	741	-
Châteaudun	maize	788	787	-	694	696	-
Châteaudun	onions	740	739	-	652	674	-
Châteaudun	peas	808	808	-	699	711	-
Châteaudun	potatoes	790	790	-	675	696	-
Châteaudun	rape (winter)	765	766	-	655	578	-
Châteaudun	sugar beets	798	796	-	684	689	-
Châteaudun	tomatoes	777	776	-	702	719	-
Châteaudun	vines	650	646	-	647	659	-
Hamburg	apples	646	647	-	602	604	-
Hamburg	beans (field)	617	615	-	527	543	-
Hamburg	cabbage	604	605	-	567	592	-
Hamburg	carrot	602	601	-	564	586	-
Hamburg	cereals (spring)	620	619	-	537	561	-
Hamburg	cereals (winter)	612	612	-	535	512	-
Hamburg	grass	609	610	-	610	610	-
Hamburg	maize	622	621	-	570	573	-
Hamburg	onions	582	580	-	533	555	-
Hamburg	peas	637	637	-	577	586	-
Hamburg	potato	625	624	-	561	573	-
Hamburg	rape (winter)	602	602	-	529	476	-
Hamburg	strawberries	610	610	-	610	610	-
Hamburg	sugar beets	627	627	-	572	567	-
Hamburg	vines	512	509	-	535	543	-
Jokioinen	apples	596	596	-	551	553	-
Jokioinen	bush berries	446	445	-	559	559	-
Jokioinen	cabbage	557	557	-	536	542	-
Jokioinen	carrots	567	563	-	532	536	-
Jokioinen	cereals (spring)	565	564	-	506	514	-
Jokioinen	cereals (winter)	562	561	-	493	469	-
Jokioinen	grass	559	559	-	559	559	-
Jokioinen	onions	532	531	-	499	508	-
Jokioinen	peas	582	582	-	531	536	-
Jokioinen	potatoes	572	572	-	530	525	-
Jokioinen	rape (summer)	554	553	-	520	520	-
Jokioinen	strawberries	559	559	-	559	559	-
Jokioinen	sugar beets	574	573	-	528	520	-
Kremsmünster	apples	710	710	-	661	664	-

Location	Crop	Potential Evapotranspiration (mm)					
		FOCUS 2009			FOCUS 2000		
		PEARL	PELMO	MACRO	PEARL	PELMO	MACRO
Kremsmünster	beans (field)	678	665	-	582	597	-
Kremsmünster	cabbage	665	661	-	625	650	-
Kremsmünster	carrots	663	680	-	621	644	-
Kremsmünster	cereals (spring)	681	671	-	594	617	-
Kremsmünster	cereals (winter)	673	670	-	589	563	-
Kremsmünster	grass	670	681	-	670	670	-
Kremsmünster	maize	682	639	-	628	630	-
Kremsmünster	onions	640	685	-	589	610	-
Kremsmünster	potatoes	686	667	-	619	630	-
Kremsmünster	rape (winter)	663	670	-	585	523	-
Kremsmünster	strawberries	670	683	-	671	670	-
Kremsmünster	sugar beets	683	560	-	630	623	-
Kremsmünster	vines	563	752	-	589	597	-
Okehampton	apples	743	734	-	701	702	-
Okehampton	beans (field)	734	721	-	585	631	-
Okehampton	cereals (spring)	722	713	-	630	653	-
Okehampton	cereals (winter)	714	710	-	628	596	-
Okehampton	grass	709	693	-	710	710	-
Okehampton	linseed	695	712	-	575	596	-
Okehampton	maize	712	741	-	663	667	-
Okehampton	peas	742	720	-	670	681	-
Okehampton	potatoes	720	702	-	659	667	-
Okehampton	rape (summer)	702	702	-	648	660	-
Okehampton	rape (winter)	701	726	-	628	553	-
Okehampton	sugar beets	727	856	-	669	660	-
Piacenza	apples	857	788	-	757	762	-
Piacenza	cereals (winter)	790	485	-	696	646	-
Piacenza	citrus	485	809	-	561	562	-
Piacenza	grass	809	839	-	769	769	-
Piacenza	maize	839	837	-	713	723	-
Piacenza	potatoes	838	800	-	683	723	-
Piacenza	rape (winter)	800	812	-	699	600	-
Piacenza	soybeans	814	811	-	694	708	-
Piacenza	sugar beets	812	832	-	703	716	-
Piacenza	sunflowers	833	807	-	621	662	-
Piacenza	tobacco	808	812	-	745	754	-
Piacenza	tomatoes	813	674	-	725	746	-
Piacenza	vines	678	1001	-	667	685	-
Porto	apples	1002	980	-	865	868	-
Porto	beans (veg)	984	952	-	724	780	-
Porto	cabbage	955	959	-	810	851	-
Porto	carrots	963	953	-	823	842	-
Porto	cereals (spring)	955	665	-	809	807	-

Table A23-4 (continued). Annual Averages of potential evapotranspiration (not reported by PRZM).

| Location | Crop | Potential Evapotranspiration (mm) | | | | | |
| | | FOCUS 2009 | | | FOCUS 2000 | | |
		PEARL	PELMO	MACRO	PEARL	PELMO	MACRO
Porto	cereals (winter)	944	942	-	779	737	-
Porto	citrus	574	575	-	640	640	-
Porto	grass	958	958	-	876	877	-
Porto	maize	973	970	-	822	824	-
Porto	onions	942	940	-	837	798	-
Porto	potatoes	972	969	-	844	824	-
Porto	rape (summer)	950	948	-	801	815	-
Porto	rape (winter)	949	948	-	754	684	-
Porto	sugar beets	946	945	-	818	815	-
Porto	tomatoes	976	975	-	816	851	-
Porto	vines	820	815	-	771	780	-
Sevilla	apples	1559	1559	-	1289	1295	-
Sevilla	cabbage	1483	1482	-	1226	1269	-
Sevilla	cereals (winter)	1479	1478	-	1202	1099	-
Sevilla	citrus	896	896	-	955	955	-
Sevilla	cotton	1492	1491	-	1230	1243	-
Sevilla	grass	1494	1494	-	1308	1308	-
Sevilla	maize	1489	1488	-	1231	1230	-
Sevilla	potatoes	1499	1499	-	1251	1230	-
Sevilla	strawberries	1493	1494	-	1308	1308	-
Sevilla	sugar beets	1479	1478	-	1234	1217	-
Sevilla	sunflowers	1475	1474	-	1179	1125	-
Sevilla	tomatoes	1477	1476	-	1272	1269	-
Sevilla	vines	1206	1202	-	1106	1164	-
Thiva	apples	1244	1245	-	1010	1013	-
Thiva	beans (veg)	1187	1184	-	880	911	-
Thiva	cabbage	1196	1196	-	1001	993	-
Thiva	carrots	1202	1200	-	944	982	-
Thiva	cereals (winter)	1182	1180	-	906	860	-
Thiva	citrus	718	718	-	747	747	-
Thiva	cotton	1199	1196	-	973	972	-
Thiva	grass	1197	1197	-	1024	1023	-
Thiva	maize	1223	1222	-	942	962	-
Thiva	onions	1173	1170	-	969	931	-
Thiva	potatoes	1219	1218	-	935	962	-
Thiva	sugar beets	1204	1202	-	949	952	-
Thiva	tobacco	1195	1196	-	997	1003	-
Thiva	tomatoes	1228	1226	-	950	993	-
Thiva	vines	979	975	-	876	911	-

Table A23-5. Annual averages of actual evapotranspiration.

Location	Crop	Actual evapotranspiration (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Châteaudun	apples	764	796	789	-	696	724	722	-
Châteaudun	cabbage	584	608	616	-	579	628	626	-
Châteaudun	carrots	572	616	615	-	587	647	644	-
Châteaudun	cereals (spring)	471	468	466	-	445	430	426	-
Châteaudun	cereals (winter)	530	509	506	-	454	441	439	-
Châteaudun	grass	718	713	736	-	695	703	702	-
Châteaudun	maize	644	676	686	-	595	624	627	-
Châteaudun	onions	549	578	579	-	535	595	593	-
Châteaudun	peas	500	479	477	-	469	439	439	-
Châteaudun	potatoes	631	645	636	-	580	614	618	-
Châteaudun	rape (winter)	533	523	522	-	452	436	435	-
Châteaudun	sugar beets	706	738	745	-	615	647	648	-
Châteaudun	tomatoes	604	629	628	-	576	621	618	-
Châteaudun	vines	604	634	635	-	615	655	655	-
Hamburg	apples	585	535	529	-	539	552	547	-
Hamburg	beans (field)	536	505	506	-	447	473	474	-
Hamburg	cabbage	507	492	490	-	468	484	481	-
Hamburg	carrot	488	494	491	-	453	484	482	-
Hamburg	cereals (spring)	555	515	526	-	474	493	492	-
Hamburg	cereals (winter)	557	523	521	-	436	473	471	-
Hamburg	grass	567	479	490	-	570	403	490	-
Hamburg	maize	525	504	505	-	475	492	493	-
Hamburg	onions	484	480	480	-	436	466	466	-
Hamburg	peas	555	518	518	-	496	496	496	-
Hamburg	potato	509	487	488	-	447	464	465	-
Hamburg	rape (winter)	535	515	513	-	439	440	438	-
Hamburg	strawberries	544	504	502	-	545	503	501	-
Hamburg	sugar beets	542	501	505	-	487	487	490	-
Hamburg	vines	414	462	462	-	384	517	516	-
Jokioinen	apples	473	441	445	-	459	439	443	-
Jokioinen	bush berries	370	354	358	-	433	400	403	-
Jokioinen	cabbage	405	387	395	-	393	379	388	-
Jokioinen	carrots	392	362	372	-	371	352	362	-
Jokioinen	cereals (spring)	426	404	407	-	396	387	391	-
Jokioinen	cereals (winter)	474	433	436	-	394	395	396	-
Jokioinen	grass	469	432	435	-	469	428	432	-
Jokioinen	onions	384	352	354	-	371	340	344	-
Jokioinen	peas	431	413	392	-	403	391	395	-
Jokioinen	potatoes	396	366	374	-	372	345	357	-
Jokioinen	rape (summer)	419	403	406	-	399	388	392	-
Jokioinen	strawberries	402	369	366	-	403	367	365	-
Jokioinen	sugar beets	419	400	407	-	394	379	387	-
Kremsmünster	apples	623	647	636	-	537	629	623	-

Table A23-5 (continued). Annual averages of actual evapotranspiration.

Location	Crop	Actual evapotranspiration (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Kremsmünster	beans (field)	575	591	586	-	486	541	538	-
Kremsmünster	cabbage	553	575	573	-	516	561	560	-
Kremsmünster	carrots	541	573	569	-	503	554	553	-
Kremsmünster	cereals (spring)	597	606	605	-	517	565	565	-
Kremsmünster	cereals (winter)	601	605	603	-	486	528	528	-
Kremsmünster	grass	600	584	588	-	601	587	587	-
Kremsmünster	maize	562	590	592	-	503	562	564	-
Kremsmünster	onions	527	550	551	-	480	532	534	-
Kremsmünster	potatoes	562	574	575	-	500	536	539	-
Kremsmünster	rape (winter)	583	598	591	-	483	490	490	-
Kremsmünster	strawberries	582	600	598	-	583	594	593	-
Kremsmünster	sugar beets	583	589	594	-	528	563	567	-
Kremsmünster	vines	455	521	521	-	397	567	567	-
Okehampton	apples	646	660	649	-	613	608	659	-
Okehampton	beans (field)	642	575	575	-	534	528	528	-
Okehampton	cereals (spring)	629	595	592	-	560	560	558	-
Okehampton	cereals (winter)	626	608	605	-	528	532	530	-
Okehampton	grass	630	580	579	-	631	579	579	-
Okehampton	linseed	606	576	578	-	503	527	527	-
Okehampton	maize	595	587	588	-	564	559	561	-
Okehampton	peas	616	573	571	-	570	545	544	-
Okehampton	potatoes	597	578	577	-	551	546	546	-
Okehampton	rape (summer)	605	592	588	-	559	588	563	-
Okehampton	rape (winter)	608	596	593	-	516	498	496	-
Okehampton	sugar beets	599	587	591	-	549	556	561	-
Piacenza	apples	799	843	835	-	707	758	758	-
Piacenza	cereals (winter)	551	557	539	-	448	480	475	-
Piacenza	citrus	478	485	485	-	533	562	562	-
Piacenza	grass	737	801	809	-	730	769	769	-
Piacenza	maize	698	767	757	-	611	684	686	-
Piacenza	potatoes	730	767	755	-	611	709	707	-
Piacenza	rape (winter)	511	517	501	-	407	427	423	-
Piacenza	soybeans	682	727	724	-	603	666	667	-
Piacenza	sugar beets	713	762	752	-	639	704	705	-
Piacenza	sunflowers	723	794	784	-	543	649	650	-
Piacenza	tobacco	648	732	722	-	634	708	709	-
Piacenza	tomatoes	644	711	692	-	592	697	695	-
Piacenza	vines	602	661	657	-	514	683	683	-
Porto	apples	887	988	986	-	648	596	590	-
Porto	beans (veg)	837	891	887	-	501	448	446	-
Porto	cabbage	758	788	802	-	507	459	459	-
Porto	carrots	682	731	747	-	473	448	449	-
Porto	cereals (spring)	605	565	563	-	500	463	461	-

Table A23-5 (continued). Annual averages of actual evapotranspiration.

Location	Crop	Actual evapotranspiration (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Porto	cereals (winter)	611	611	603	-	471	477	470	-
Porto	citrus	535	575	575	-	547	519	519	-
Porto	grass	860	945	956	-	594	531	531	-
Porto	maize	795	891	902	-	523	492	494	-
Porto	onions	491	565	566	-	403	416	414	-
Porto	potatoes	548	624	620	-	435	449	445	-
Porto	rape (summer)	733	832	826	-	556	532	529	-
Porto	rape (winter)	640	620	613	-	466	469	463	-
Porto	sugar beets	693	725	720	-	565	537	532	-
Porto	tomatoes	820	855	854	-	525	462	462	-
Porto	vines	691	792	792	-	578	577	576	-
Sevilla	apples	1377	1323	1314	-	1155	1118	1153	-
Sevilla	cabbage	934	961	1000	-	760	710	751	-
Sevilla	cereals (winter)	511	374	372	-	435	311	312	-
Sevilla	citrus	895	896	896	-	950	955	955	-
Sevilla	cotton	695	663	669	-	787	727	792	-
Sevilla	grass	1304	1424	1471	-	1159	1135	1175	-
Sevilla	maize	805	772	791	-	802	670	735	-
Sevilla	potatoes	563	544	544	-	505	478	493	-
Sevilla	strawberries	985	1160	1153	-	881	729	761	-
Sevilla	sugar beets	723	654	658	-	676	683	694	-
Sevilla	sunflowers	709	724	742	-	657	655	717	-
Sevilla	tomatoes	579	578	580	-	639	681	719	-
Sevilla	vines	1035	1097	1094	-	979	1090	1113	-
Thiva	apples	1074	1129	1121	-	823	947	960	-
Thiva	beans (veg)	818	836	847	-	651	653	635	-
Thiva	cabbage	474	486	498	-	593	613	632	-
Thiva	carrots	817	829	831	-	692	705	733	-
Thiva	cereals (winter)	445	403	402	-	385	317	316	-
Thiva	citrus	689	718	718	-	541	746	746	-
Thiva	cotton	671	701	704	-	718	748	776	-
Thiva	grass	1044	1119	1138	-	897	857	870	-
Thiva	maize	902	966	970	-	663	691	722	-
Thiva	onions	438	537	540	-	566	630	654	-
Thiva	potatoes	750	748	751	-	701	663	691	-
Thiva	sugar beets	883	909	912	-	716	801	824	-
Thiva	tobacco	877	915	932	-	768	757	788	-
Thiva	tomatoes	916	932	940	-	716	721	754	-
Thiva	vines	822	863	861	-	630	895	897	-

Table A23-6. Annual averages of percolation past 1 m.

Location	Crop	Percolation past 1 m (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Châteaudun	apples	236	226	232	-	473	416	398	-
Châteaudun	cabbage	249	239	241	-	354	221	232	-
Châteaudun	carrots	251	204	204	-	346	180	192	-
Châteaudun	cereals (spring)	178	180	182	-	203	174	176	-
Châteaudun	cereals (winter)	119	140	142	-	194	177	179	-
Châteaudun	grass	269	267	244	-	255	242	245	-
Châteaudun	maize	269	227	228	-	376	199	207	-
Châteaudun	onions	212	209	209	-	398	261	270	-
Châteaudun	peas	149	170	171	-	179	159	160	-
Châteaudun	potatoes	216	214	225	-	380	202	211	-
Châteaudun	rape (winter)	115	128	129	-	197	191	195	-
Châteaudun	sugar beets	337	240	242	-	382	273	281	-
Châteaudun	tomatoes	221	197	198	-	357	230	240	-
Châteaudun	vines	287	256	254	-	534	481	498	-
Hamburg	apples	201	254	259	-	369	274	275	-
Hamburg	beans (field)	250	281	280	-	339	260	257	-
Hamburg	cabbage	280	294	297	-	318	261	260	-
Hamburg	carrot	298	293	295	-	334	259	259	-
Hamburg	cereals (spring)	231	271	261	-	312	246	245	-
Hamburg	cereals (winter)	230	265	267	-	362	289	295	-
Hamburg	grass	219	307	297	-	217	381	294	-
Hamburg	maize	261	283	282	-	329	239	239	-
Hamburg	onions	303	307	307	-	351	273	271	-
Hamburg	peas	231	268	268	-	290	240	237	-
Hamburg	potato	278	299	299	-	340	264	262	-
Hamburg	rape (winter)	252	273	275	-	361	332	337	-
Hamburg	strawberries	242	282	284	-	241	273	274	-
Hamburg	sugar beets	245	286	282	-	309	260	256	-
Hamburg	vines	372	326	326	-	457	334	340	-
Jokioinen	apples	177	211	207	-	238	197	202	-
Jokioinen	bush berries	280	296	292	-	218	230	228	-
Jokioinen	cabbage	244	263	255	-	257	183	171	-
Jokioinen	carrots	259	288	278	-	279	209	198	-
Jokioinen	cereals (spring)	224	247	243	-	254	167	158	-
Jokioinen	cereals (winter)	176	217	214	-	256	204	200	-
Jokioinen	grass	181	218	216	-	181	204	200	-
Jokioinen	onions	265	298	296	-	279	212	204	-
Jokioinen	peas	220	238	258	-	247	156	147	-
Jokioinen	potatoes	254	284	276	-	278	191	179	-
Jokioinen	rape (summer)	231	247	244	-	251	169	160	-
Jokioinen	strawberries	248	281	284	-	247	244	245	-
Jokioinen	sugar beets	231	250	244	-	256	188	176	-
Kremsmünster	apples	273	255	265	-	447	301	297	-

582

Table A23-6 (continued). Annual averages of percolation past 1 m.

Location	Crop	Percolation past 1 m (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Kremsmünster	beans (field)	320	308	313	-	409	214	220	-
Kremsmünster	cabbage	342	325	327	-	381	226	227	-
Kremsmünster	carrots	354	327	330	-	393	222	224	-
Kremsmünster	cereals (spring)	299	294	294	-	379	213	214	-
Kremsmünster	cereals (winter)	295	296	297	-	419	272	282	-
Kremsmünster	grass	295	316	312	-	298	293	293	-
Kremsmünster	maize	333	310	308	-	406	168	172	-
Kremsmünster	onions	369	350	348	-	415	244	243	-
Kremsmünster	potatoes	333	325	324	-	396	193	194	-
Kremsmünster	rape (winter)	313	303	309	-	423	324	333	-
Kremsmünster	strawberries	313	299	301	-	316	243	246	-
Kremsmünster	sugar beets	313	311	306	-	378	230	228	-
Kremsmünster	vines	436	381	379	-	518	398	407	-
Okehampton	apples	392	380	390	-	516	407	397	-
Okehampton	beans (field)	396	463	463	-	504	357	358	-
Okehampton	cereals (spring)	410	443	446	-	478	327	331	-
Okehampton	cereals (winter)	412	430	433	-	510	417	422	-
Okehampton	grass	408	458	459	-	407	442	442	-
Okehampton	linseed	432	462	460	-	535	376	376	-
Okehampton	maize	442	451	450	-	475	287	289	-
Okehampton	peas	422	465	467	-	468	328	330	-
Okehampton	potatoes	440	460	461	-	487	301	305	-
Okehampton	rape (summer)	433	446	449	-	478	298	327	-
Okehampton	rape (winter)	429	442	445	-	521	472	476	-
Okehampton	sugar beets	439	451	446	-	489	350	346	-
Piacenza	apples	214	464	472	-	672	498	499	-
Piacenza	cereals (winter)	307	301	319	-	410	325	331	-
Piacenza	citrus	442	614	651	-	809	690	698	-
Piacenza	grass	337	514	506	-	496	456	457	-
Piacenza	maize	346	490	501	-	611	468	476	-
Piacenza	potatoes	349	425	441	-	627	450	462	-
Piacenza	rape (winter)	346	341	357	-	450	394	399	-
Piacenza	soybeans	393	471	482	-	620	465	481	-
Piacenza	sugar beets	312	389	401	-	610	478	484	-
Piacenza	sunflowers	310	467	482	-	679	488	498	-
Piacenza	tobacco	368	484	497	-	589	420	433	-
Piacenza	tomatoes	321	381	402	-	593	400	412	-
Piacenza	vines	352	488	491	-	801	591	600	-
Porto	apples	631	674	674	-	541	525	543	-
Porto	beans (veg)	604	674	681	-	604	421	417	-
Porto	cabbage	651	761	760	-	598	476	475	-
Porto	carrots	650	719	718	-	628	453	451	-
Porto	cereals (spring)	525	585	587	-	604	417	413	-

Table A23-6 (continued). Annual averages of percolation past 1 m.

Location	Crop	Percolation past 1 m (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Porto	cereals (winter)	513	540	548	-	624	500	504	-
Porto	citrus	760	887	886	-	704	596	610	-
Porto	grass	635	746	735	-	519	579	578	-
Porto	maize	640	652	654	-	588	352	349	-
Porto	onions	638	678	680	-	690	459	458	-
Porto	potatoes	651	664	671	-	661	398	398	-
Porto	rape (summer)	572	630	638	-	557	346	343	-
Porto	rape (winter)	486	532	539	-	629	572	577	-
Porto	sugar beets	510	604	610	-	547	338	340	-
Porto	tomatoes	577	656	662	-	583	416	411	-
Porto	vines	681	671	670	-	670	541	557	-
Sevilla	apples	203	92	100	-	462	67	86	-
Sevilla	cabbage	97	155	155	-	237	24	27	-
Sevilla	cereals (winter)	-18	119	121	-	58	81	85	-
Sevilla	citrus	413	330	329	-	648	260	312	-
Sevilla	cotton	39	105	106	-	311	17	23	-
Sevilla	grass	215	240	193	-	205	122	129	-
Sevilla	maize	68	151	149	-	296	37	43	-
Sevilla	potatoes	108	154	157	-	253	45	56	-
Sevilla	strawberries	53	245	253	-	116	104	112	-
Sevilla	sugar beets	71	137	141	-	277	75	102	-
Sevilla	sunflowers	100	129	130	-	441	24	32	-
Sevilla	tomatoes	76	95	98	-	357	15	26	-
Sevilla	vines	313	158	159	-	566	99	129	-
Thiva	apples	172	120	126	-	517	186	192	-
Thiva	beans (veg)	153	179	178	-	374	97	109	-
Thiva	cabbage	209	228	224	-	432	125	124	-
Thiva	carrots	116	162	162	-	333	93	97	-
Thiva	cereals (winter)	54	97	98	-	115	117	116	-
Thiva	citrus	243	318	317	-	725	394	419	-
Thiva	cotton	89	110	111	-	387	78	87	-
Thiva	grass	181	237	218	-	217	216	220	-
Thiva	maize	102	133	136	-	441	71	76	-
Thiva	onions	119	180	181	-	459	114	122	-
Thiva	potatoes	105	145	146	-	365	93	98	-
Thiva	sugar beets	79	107	109	-	451	115	134	-
Thiva	tobacco	174	201	199	-	336	93	96	-
Thiva	tomatoes	109	147	147	-	309	90	95	-
Thiva	vines	191	123	124	-	654	295	325	-

Table A23-7. Annual averages of percolation past the bottom of the soil column.

Location	Crop	Percolation past the Bottom of the Soil Column (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Châteaudun	apples	236	222	229	-	275	235	238	-
Châteaudun	cabbage	249	239	241	-	354	221	232	-
Châteaudun	carrots	251	204	204	-	346	180	192	-
Châteaudun	cereals (spring)	178	180	182	-	203	174	176	-
Châteaudun	cereals (winter)	118	140	142	-	194	177	179	-
Châteaudun	grass	269	249	244	-	255	242	245	-
Châteaudun	maize	269	227	228	-	376	199	207	-
Châteaudun	onions	212	209	209	-	398	261	270	-
Châteaudun	peas	149	170	171	-	179	159	160	-
Châteaudun	potatoes	216	214	225	-	380	202	211	-
Châteaudun	rape (winter)	115	126	127	-	197	191	193	-
Châteaudun	sugar beets	337	238	240	-	382	273	279	-
Châteaudun	tomatoes	221	197	198	-	357	230	240	-
Châteaudun	vines	287	250	251	-	356	304	305	-
Hamburg	apples	201	259	258	-	247	232	237	-
Hamburg	beans (field)	250	281	280	-	339	260	257	-
Hamburg	cabbage	280	294	297	-	318	261	260	-
Hamburg	carrot	298	293	295	-	334	259	259	-
Hamburg	cereals (spring)	231	271	261	-	312	246	245	-
Hamburg	cereals (winter)	230	264	266	-	351	289	291	-
Hamburg	grass	219	323	297	-	217	381	294	-
Hamburg	maize	261	283	281	-	312	236	233	-
Hamburg	onions	303	307	307	-	351	273	271	-
Hamburg	peas	231	268	268	-	290	240	237	-
Hamburg	potato	278	299	299	-	340	264	262	-
Hamburg	rape (winter)	252	271	274	-	347	331	333	-
Hamburg	strawberries	242	282	284	-	241	273	274	-
Hamburg	sugar beets	245	285	282	-	299	259	253	-
Hamburg	vines	372	342	324	-	402	265	266	-
Jokioinen	apples	177	210	206	-	191	188	187	-
Jokioinen	bush berries	280	296	292	-	218	230	228	-
Jokioinen	cabbage	244	263	255	-	257	183	171	-
Jokioinen	carrots	259	288	278	-	279	209	198	-
Jokioinen	cereals (spring)	224	247	243	-	254	167	158	-
Jokioinen	cereals (winter)	176	217	214	-	256	204	200	-
Jokioinen	grass	181	233	216	-	181	204	200	-
Jokioinen	onions	265	298	296	-	279	212	204	-
Jokioinen	peas	220	238	258	-	247	156	147	-
Jokioinen	potatoes	254	284	276	-	278	191	179	-
Jokioinen	rape (summer)	231	247	244	-	251	169	160	-
Jokioinen	strawberries	248	288	284	-	247	244	245	-
Jokioinen	sugar beets	231	250	244	-	256	188	176	-
Kremsmünster	apples	273	222	263	-	356	241	248	-

Table A23-7 (continued). Annual averages of percolation past the bottom of the soil column.

Location	Crop	Percolation past the Bottom of the Soil Column (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Kremsmünster	beans (field)	320	266	313	-	409	214	220	-
Kremsmünster	cabbage	342	308	327	-	381	226	227	-
Kremsmünster	carrots	354	325	330	-	393	222	224	-
Kremsmünster	cereals (spring)	299	327	294	-	379	213	214	-
Kremsmünster	cereals (winter)	295	294	296	-	409	271	277	-
Kremsmünster	grass	295	294	312	-	298	293	293	-
Kremsmünster	maize	333	344	307	-	393	164	164	-
Kremsmünster	onions	369	309	348	-	415	244	243	-
Kremsmünster	potatoes	333	350	324	-	396	193	194	-
Kremsmünster	rape (winter)	313	325	308	-	410	323	328	-
Kremsmünster	strawberries	313	302	301	-	316	243	246	-
Kremsmünster	sugar beets	313	300	306	-	368	228	223	-
Kremsmünster	vines	436	310	378	-	489	302	303	-
Okehampton	apples	392	393	388	-	425	407	356	-
Okehampton	beans (field)	396	381	463	-	504	357	358	-
Okehampton	cereals (spring)	410	463	446	-	478	327	331	-
Okehampton	cereals (winter)	412	443	433	-	510	417	422	-
Okehampton	grass	408	430	459	-	407	442	442	-
Okehampton	linseed	432	486	460	-	535	376	376	-
Okehampton	maize	442	462	450	-	475	287	289	-
Okehampton	peas	422	451	467	-	468	328	330	-
Okehampton	potatoes	440	465	461	-	487	301	305	-
Okehampton	rape (summer)	433	460	449	-	478	298	327	-
Okehampton	rape (winter)	429	446	445	-	521	472	476	-
Okehampton	sugar beets	439	442	446	-	489	350	346	-
Piacenza	apples	214	451	470	-	512	458	459	-
Piacenza	cereals (winter)	307	461	318	-	410	325	330	-
Piacenza	citrus	442	301	613	-	685	655	655	-
Piacenza	grass	337	613	506	-	496	456	457	-
Piacenza	maize	346	496	501	-	611	468	475	-
Piacenza	potatoes	349	489	441	-	627	450	462	-
Piacenza	rape (winter)	346	425	357	-	450	394	399	-
Piacenza	soybeans	393	341	482	-	620	465	481	-
Piacenza	sugar beets	312	471	401	-	610	478	484	-
Piacenza	sunflowers	310	389	481	-	679	488	498	-
Piacenza	tobacco	368	466	496	-	589	420	432	-
Piacenza	tomatoes	321	483	402	-	593	400	411	-
Piacenza	vines	352	380	490	-	704	529	530	-
Porto	apples	631	480	672	-	472	505	513	-
Porto	beans (veg)	604	661	681	-	604	421	417	-
Porto	cabbage	651	674	760	-	598	476	475	-
Porto	carrots	650	761	718	-	628	453	451	-
Porto	cereals (spring)	525	719	587	-	604	417	413	-

Table A23-7 (continued). Annual averages of percolation past the bottom of the soil column.

Location	Crop	Percolation past the Bottom of the Soil Column (mm)							
		FOCUS 2009				FOCUS 2000			
		PEARL	PELMO	PRZM	MACRO	PEARL	PELMO	PRZM	MACRO
Porto	cereals (winter)	513	539	547	-	624	500	502	-
Porto	citrus	760	884	885	-	559	581	582	-
Porto	grass	635	735	735	-	519	579	578	-
Porto	maize	640	652	654	-	588	352	349	-
Porto	onions	638	678	680	-	690	459	458	-
Porto	potatoes	651	664	671	-	661	398	398	-
Porto	rape (summer)	572	630	638	-	557	346	343	-
Porto	rape (winter)	486	530	537	-	629	572	576	-
Porto	sugar beets	510	602	608	-	547	338	338	-
Porto	tomatoes	576	656	662	-	583	416	411	-
Porto	vines	681	654	668	-	535	524	527	-
Sevilla	apples	203	69	94	-	167	31	37	-
Sevilla	cabbage	97	155	155	-	237	24	27	-
Sevilla	cereals (winter)	-18	119	121	-	58	81	85	-
Sevilla	citrus	413	326	326	-	372	174	201	-
Sevilla	cotton	39	105	106	-	311	17	23	-
Sevilla	grass	215	224	193	-	205	122	129	-
Sevilla	maize	68	151	149	-	296	37	43	-
Sevilla	potatoes	108	154	157	-	253	45	56	-
Sevilla	strawberries	53	245	253	-	116	104	112	-
Sevilla	sugar beets	71	137	141	-	277	75	102	-
Sevilla	sunflowers	100	129	130	-	441	24	32	-
Sevilla	tomatoes	76	95	98	-	357	15	26	-
Sevilla	vines	313	141	155	-	344	53	64	-
Thiva	apples	172	109	124	-	337	145	151	-
Thiva	beans (veg)	153	179	178	-	374	97	109	-
Thiva	cabbage	209	228	224	-	432	125	124	-
Thiva	carrots	116	162	162	-	333	93	97	-
Thiva	cereals (winter)	54	97	98	-	115	117	116	-
Thiva	citrus	243	315	315	-	618	336	348	-
Thiva	cotton	89	110	111	-	387	78	87	-
Thiva	grass	181	225	218	-	217	216	220	-
Thiva	maize	102	133	136	-	441	71	76	-
Thiva	onions	119	180	181	-	459	114	122	-
Thiva	potatoes	105	145	146	-	365	93	98	-
Thiva	sugar beets	79	107	109	-	451	115	134	-
Thiva	tobacco	174	201	199	-	336	93	96	-
Thiva	tomatoes	109	147	147	-	309	90	95	-
Thiva	vines	191	114	122	-	529	190	200	-

APPENDIX 24. REVIEW OF PROCEDURE FOR ESTIMATING INTERCEPTION OF PESTICIDE BY PLANTS

FOCUS (2000) decided to estimate interception of pesticide application by the plant canopy using experimental measurements available in the literature. At that time the PESTLA model (recommended for use by FOCUS 2000) did not contain a routine for estimating crop interception. The PEARL model has superseded PESTLA and can estimate interception automatically. All the models recommended by FOCUS for estimating ground water concentrations can now estimate interception; so the work group reviewed whether the Tier I recommendations should be changed to allow them to do so.

Current Method of Estimating Interception.

Look up tables are used to estimate the amount of interception of pesticide by the crop canopy during application. These tables give percentage interception for various growth stages of major crops. The appropriate growth stage during application is selected, and the amount of pesticide reaching the soil surface during application is calculated by:

(1 - %interception/100)*application rate.

The data in the lookup tables were derived from experimental measurements. Crops for which there were no data had interception estimated by the GLEAMS model on the basis of Leaf Area Index (LAI). The FOCUS Groundwater Scenarios Workgroup used conservative estimates of interception, i.e. using values for earlier growth stages where a range was specified and using values towards the lower end of the measured range. Interception was never allowed to exceed 90%.

Estimation of Interception by FOCUS Models.

All of the FOCUS models (MACRO, PEARL, PELMO, PRZM) can estimate crop growth by assuming that growth is linear between certain crop growth stages. PELMO and PRZM assume that interception is zero at emergence, maximum at maturity and varies linearly in-between. Interception stays at the maximum value between maturity and harvest, interception is expressed as a percentage interception of applied spray.

MACRO and PEARL have more detailed crop growth models. Both models calculate interception on the basis of leaf area index (LAI) rather than percentage interception of the application. MACRO requires the input of the LAI at emergence (generally a very low

588

number), at maximum LAI and at harvest; a day number for each event is also required. The LAI on any particular day D between emergence and maximum LAI is given by:

$$LAI = LAI_{min} + (LAI_{max} - LAI_{min}) \left[\frac{D - D_{min}}{D_{max} - D_{min}} \right]^x$$

where x is an exponent specified by the user. The above equation shows that LAI varies according to the interval between maximum and minimum LAI in a similar way to how interception is calculated between emergence and maturity in PELMO, except the exponent is rarely 1.0 (for spring cereals in the Châteaudun scenario it is 2.0) meaning that LAI does not vary linearly with time. MACRO uses a similar routine to calculate the decrease in LAI between maturity and harvest due to senescence.

PEARL calculates LAI on the basis of development stage. Development can be simulated in two ways: either input directly by the user as a function of time (with linear interpolation between time points) or dependent upon a temperature sum. The fraction of interception of pesticide is dependent upon the LAI, interception is assumed to be LAI/3 with a maximum of 100%.

Within FOCUS, models have been harmonised for emergence, maturity (max LAI) and harvest dates for all crops in all scenarios. Figure A24-1 shows how FOCUS-PELMO and FOCUS-PEARL would calculate crop growth stage for spring cereals in Germany. The length of the growing season was taken from the FOCUS Hamburg scenario, growth stage BBCH 9 was assumed to represent emergence, growth stage 90 to represent harvest. The model estimates of growth stage are compared to typical values for oats and spring barley measured over the period 1962-1996 at the Berlin-Dahlem experimental station (Chemielewski, 2003).
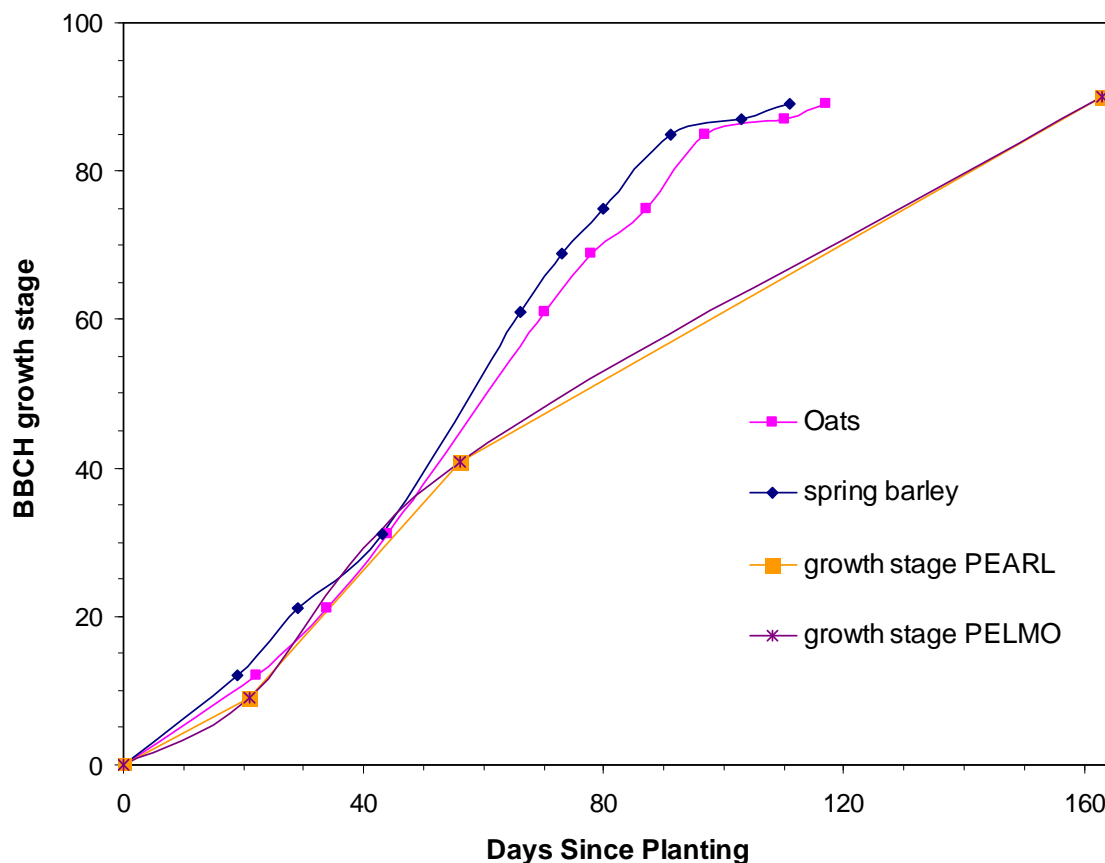
Figure A24-1. BBCH growth stage for spring cereals calculated by PEARL and PELMO for the Hamburg scenario opposite average measurements of growth stage at the Berlin-Dahlen experimental station over the period 1962 – 1996 (from Chemielewski 2003)

Figure A24-1 shows that both models predict early growth stages well, however there is some divergence for later growth stages. The length of the growing season is much larger in the FOCUS models than measured for oats and barley, which may be because the FOCUS growing season was parameterised for wheat rather than these crops. Nevertheless Figure A24-1 shows that linear crop development is a simplified assumption for growth stage.

Figure A24-2 shows the interception that the PELMO and PEARL models would predict for the Hamburg scenario. The PELMO values were based upon a maximum interception of 90% at maturity (FOCUS value for spring cereals) and the length of the period to maturity (maximum LAI). The PEARL values were derived from the LAI. The interception for the measured growth stages of spring barley for the period 1962 – 1996 is also shown, assuming the interception values provided by FOCUS.

Figure A24-2 demonstrates that calculating interception from LAI and linearly according to growth stage will yield different results. Also the fit between model predictions and experimental measurements is poor. For early growth stages, the experimental data show higher values of interception than the models, probably because the models are based upon the longer growing season of wheat; for latter growth stages the models over-predict interception because of the conservative assumption of 70% interception up to growth stage 90 by FOCUS. In any case, the assumption of linear interception with growth stage does not fit the experimental data well.
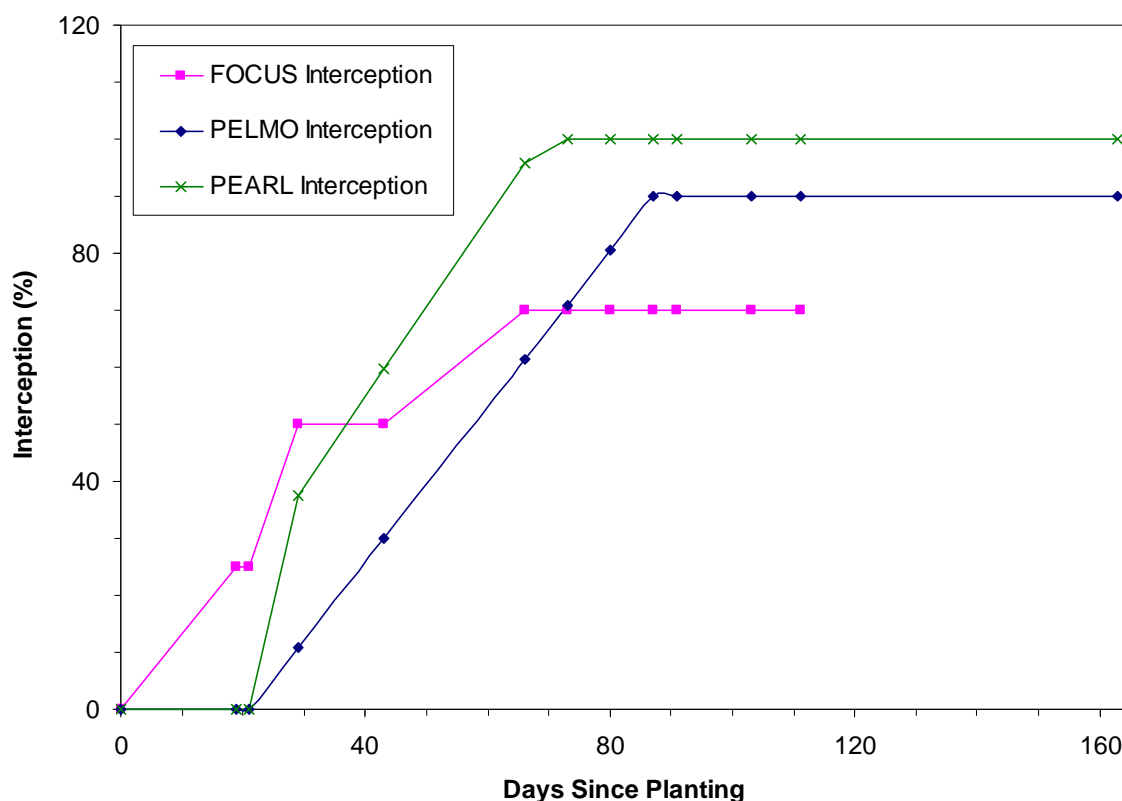
Figure A24-2. Interception calculated by: PELMO and PEARL models and according to FOCUS for growth stages of spring barley measured at the Berlin-Dahlen experimental station over 1961- 1996 (Chemielewski 2003).

Conclusions: estimation of interception

Allowing models to calculate interception means that different models may calculate different interception values for the same crop at the same time. The initial soil burden following application will therefore differ between models, potentially leading to different leachate

concentrations. Note that in this comparison between PEARL and PELMO the same maturity dates were used, and linear crop development was assumed for both models.

The models calculate interception in different ways: PEARL uses a time-dependent specification based upon LAI; PELMO assumes that interception is linear with time according to growth stage; MACRO uses a function to calculate interception based upon LAI that may vary from crop to crop. Considerable effort would therefore be required to harmonise interception in these models for all crops and for all scenarios.

The models did not reproduce the interception derived from experimental data well. This was in part because they assume they use the length of the growing season from a different crop and in part because of conservative assumptions used by FOCUS. The length of the growing season will differ between different crops within the same general group (e.g. such as cereals), so a large amount of extra work would be required to adequately model interception with all of the FOCUS models.

The FOCUS Groundwater Scenarios Workgroup spent considerable effort determining crop interception from experimental measurements available in the literature, and were conservative in their assumptions. Basing interception according to growth stage from experimental measurements is a simple way of harmonising the initial burden to the soil and is independent of the length of the growing season. Models can only approximate these measurements by using simplified assumptions or by inputting the experimental data directly.

Allowing models to calculate interception therefore presents no benefits either in terms of accuracy or consistency. As stated in FOCUS (2000): "For reasons of consistency, simplicity and accuracy, FOCUS recommend that the internal interception routines in all models are disabled and the application rate is manually corrected for interception".

Therefore, the work group proposed that no changes be made to the current method of estimating interception.

References

Chemielewski F.M. 2003. Phenology and Agriculture, Agrarmeteorologishe Schriften, Heft 12, Landwirtsschaftlich-Gärtnerische Fakultät, Insitut für Pfanzenbauwissenschaften, Humboldt-Universität zu Berlin.

FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000 rev.2, 202pp.

APPENDIX 25. COMPARISON OF DIFFERENT OBJECT FUNCTIONS FOR THE EVALUATION OF KINETIC SORPTION EXPERIMENTS

C. Kley and K. Hammel

In general, four variables are available from time-dependant sorption studies, which can be fitted to evaluate kinetic sorption parameters: M_t, $C_{l\,des}$, S_{eq}, S_{neq}.

This leads to five meaningful combinations which could be used as an object function:

M_t - $C_{l\,des}$, M_t - S_{eq}, M_t - S_{neq}, $C_{l\,des}$ - S_{neq}, S_{eq} - S_{neq}

There should be no difference between the fits to the different object functions with respect to reliability and uncertainty of parameters. Thus, slight deviations of estimated parameters and coefficients of variation should be coincidental.

However, fits to different object functions can be comparable only under the assumption that the parameters are mathematically reliable, i.e. significantly different from 0 (t-test). In less stable experimental systems, with low χ^2 errors and low significance, the estimated parameters may differ significantly between the different fit approaches.

To examine this hypothesis of equivalence, a **numerical experiment** was carried out, to compare the results of the main approaches used to date, the M_{total} - $C_{l\,des}$ and the S_{eq} - S_{neq} object functions.

A kinetic parameter set was chosen corresponding to the example case in Appendix 6 to represent the "true" time curves of S_{eq}, S_{neq}, M_{total} and $C_{l\,des}$. To introduce statistical error into these variables, the kinetic parameters were defined as random variables with a known distribution. For this purpose f_{ne} was defined as normal distributed random variable, with **mean = 0.6** and **standard deviation = 0.06.** 13 data sets were created randomly from 104 Latin Hypercube samples (8 time points per curve) of the f_{ne} distribution, using MatLab (2007). Thus every data set of eight S_{eq}, S_{neq}, M_{total} and $C_{l\,des}$ values was generated with eight different f_{ne} . For simplicity the remaining parameters have been fixed at their mean value. These 13 data sets are presented in Table A25-1.

Table A25-1. The 13 randomly generated data sets used in the numerical experiment.

	Time	S_eq	S_neq	M_total	Cl_des	fne, used for prediction of time curves / time points
	d	µg/g	µg/g	µg	µg/mL	
1	0	0.9509	0	0.5	0.2422	0.6315
	7	0.8575	0.0476	0.4744	0.2165	0.6244
	14	0.7782	0.085	0.4512	0.1949	0.6127
	28	0.6592	0.1287	0.4103	0.1628	0.5526
	61	0.4631	0.1886	0.3369	0.111	0.5564
	90	0.3566	0.2089	0.291	0.0836	0.5873
	120	0.2957	0.1868	0.248	0.0682	0.5325
	148	0.2484	0.178	0.2187	0.0565	0.5477
2	0	0.9509	0	0.5	0.2422	0.6847
	7	0.8581	0.0469	0.4744	0.2167	0.6147
	14	0.7887	0.0733	0.4509	0.1977	0.5246
	28	0.6492	0.1407	0.411	0.1601	0.609
	61	0.4664	0.1838	0.3362	0.1119	0.5399
	90	0.371	0.1831	0.2857	0.0873	0.5002
	120	0.2884	0.2043	0.2529	0.0664	0.5955
	148	0.2396	0.2074	0.2288	0.0543	0.6651
3	0	0.9509	0	0.5	0.2422	0.6205
	7	0.8557	0.0495	0.4744	0.216	0.6502
	14	0.7873	0.0749	0.451	0.1974	0.5363
	28	0.6541	0.1348	0.4107	0.1614	0.5812
	61	0.4559	0.199	0.3383	0.1091	0.593
	90	0.3667	0.1907	0.2872	0.0862	0.5255
	120	0.298	0.1816	0.2465	0.0688	0.5141
	148	0.2398	0.2069	0.2286	0.0543	0.6627
4	0	0.9509	0	0.5	0.2422	0.6113
	7	0.8613	0.0434	0.4744	0.2175	0.5685
	14	0.7726	0.0913	0.4514	0.1934	0.6602
	28	0.6468	0.1435	0.4112	0.1595	0.6223
	61	0.4633	0.1883	0.3368	0.1111	0.5555
	90	0.3422	0.2349	0.2964	0.0799	0.6808
	120	0.2848	0.213	0.2553	0.0655	0.6283
	148	0.2379	0.2132	0.2308	0.0539	0.6892
5	0	0.9509	0	0.5	0.2422	0.6723
	7	0.8615	0.0432	0.4743	0.2176	0.5655
	14	0.7897	0.0722	0.4509	0.198	0.5162
	28	0.6495	0.1403	0.411	0.1602	0.607
	61	0.4562	0.1986	0.3382	0.1092	0.5915
	90	0.3604	0.2021	0.2896	0.0845	0.5637
	120	0.2835	0.2161	0.2562	0.0652	0.6398
	148	0.2378	0.2138	0.2311	0.0538	0.692
6	0	0.9509	0	0.5	0.2422	0.5772
	7	0.8617	0.043	0.4743	0.2177	0.563
	14	0.7801	0.0829	0.4512	0.1954	0.5968
	28	0.6413	0.1501	0.4115	0.158	0.654
	61	0.4622	0.1899	0.3371	0.1108	0.561
	90	0.3659	0.1922	0.2875	0.086	0.5303
	120	0.2877	0.2061	0.2534	0.0662	0.6023
	148	0.2438	0.1936	0.2241	0.0553	0.6086
7	0	0.9509	0	0.5	0.2422	0.6371
	7	0.8609	0.0439	0.4744	0.2174	0.5748
	14	0.7796	0.0834	0.4512	0.1953	0.6007
	28	0.6537	0.1352	0.4107	0.1613	0.5832
	61	0.4538	0.2021	0.3387	0.1086	0.6039
	90	0.3401	0.2387	0.2972	0.0794	0.695
	120	0.291	0.198	0.2511	0.067	0.5725
	148	0.2515	0.168	0.2153	0.0572	0.5097

Table A25-1 (continued). The 13 randomly generated data sets used in the numerical experiment.

	Time	S_eq	S_neq	M_total	Cl_des	fne, used for prediction of time curves / time points
8	0	0.9509	0	0.5	0.2422	0.6356
	7	0.862	0.0427	0.4743	0.2177	0.5588
	14	0.778	0.0852	0.4513	0.1948	0.6142
	28	0.6559	0.1326	0.4105	0.1619	0.5708
	61	0.4461	0.2132	0.3402	0.1066	0.644
	90	0.3471	0.2259	0.2945	0.0812	0.6478
	120	0.2881	0.2051	0.2531	0.0663	0.5986
	148	0.2609	0.1372	0.2049	0.0595	0.3997
9	0	0.9509	0	0.5	0.2422	0.6213
	7	0.8514	0.0542	0.4745	0.2148	0.7134
	14	0.7716	0.0923	0.4515	0.1931	0.6684
	28	0.6718	0.1136	0.4094	0.1662	0.4829
	61	0.4536	0.2023	0.3387	0.1085	0.6046
	90	0.3596	0.2033	0.2898	0.0844	0.5682
	120	0.2937	0.1917	0.2493	0.0677	0.5498
	148	0.2505	0.171	0.2164	0.057	0.5212
10	0	0.9509	0	0.5	0.2422	0.6259
	7	0.8602	0.0446	0.4744	0.2173	0.5843
	14	0.7777	0.0855	0.4513	0.1948	0.6166
	28	0.6527	0.1365	0.4107	0.1611	0.5892
	61	0.4584	0.1953	0.3378	0.1098	0.58
	90	0.3494	0.2218	0.2937	0.0818	0.633
	120	0.2816	0.2205	0.2574	0.0647	0.6571
	148	0.2322	0.2328	0.2376	0.0525	0.7745
11	0	0.9509	0	0.5	0.2422	0.496
	7	0.8625	0.0422	0.4743	0.2179	0.5516
	14	0.7714	0.0927	0.4515	0.193	0.6708
	28	0.6532	0.1358	0.4107	0.1612	0.586
	61	0.4771	0.1684	0.3342	0.1146	0.488
	90	0.3499	0.221	0.2935	0.0819	0.63
	120	0.2771	0.2315	0.2606	0.0636	0.7002
	148	0.2404	0.2049	0.228	0.0545	0.6548
12	0	0.9509	0	0.5	0.2422	0.7313
	7	0.8563	0.0488	0.4744	0.2162	0.6415
	14	0.7657	0.099	0.4516	0.1915	0.7191
	28	0.6524	0.1369	0.4108	0.161	0.5908
	61	0.4669	0.1831	0.3361	0.112	0.5375
	90	0.3549	0.2119	0.2916	0.0832	0.5978
	120	0.2797	0.2253	0.2588	0.0642	0.6755
	148	0.2489	0.1765	0.2182	0.0566	0.5417
13	0	0.9509	0	0.5	0.2422	0.6488
	7	0.8609	0.0438	0.4744	0.2174	0.5741
	14	0.7744	0.0892	0.4514	0.1939	0.6445
	28	0.6606	0.127	0.4102	0.1632	0.5445
	61	0.4509	0.2062	0.3393	0.1078	0.6186
	90	0.3778	0.1709	0.2832	0.089	0.4609
	120	0.2904	0.1995	0.2515	0.0669	0.578
	148	0.2419	0.1999	0.2263	0.0548	0.6342

These 13 data sets were used to optimise the sorption kinetic parameters using both object functions, where only f_{ne} was fitted, as it was the only uncertain parameter. The other parameters were fixed to their known "true" values.

All optimisations were done using the software MatLab (MatLab, 2007).

Model parameters and initial values are summarised in Table A25-2. The optimisation results for f_{ne} are shown in Figure 23-1 and Tables A25-3 and A25-4. Pairwise comparisons between optimised f_{ne} and its coefficient of variation (standard deviation of parameter / optimised f_{ne}) are shown in Figures A25-2 and A25-3. Visual examples of the fits for data sets 5 and 13 are provided in Figures A25-4 and 5 and for all data sets in Figure A25-6.

Table A25-2. Model parameters, initial values (= final value if fixed), similar to the example case in Appendix 6.

| Name	Value				
1/n	0.9		fix		Freundlich exponent
M_app	0.5	μg	fix		Applied substance mass [μg]
M_soil	0.5	g	fix		Soil dry mass [g]
theta_g	0.1492	g/g	fix		Gravimetric water content during incubation [g water/g soil]
Vw_add	0.5	mL	fix		Water volume added for desorption [mL]
Kf_eq	2.586	L/kg	fix		Freundlich coefficient, in equilibrium domain [L/kg]
k_t	0.0077019	1/d	fix	= DT50 90 d	Degradation rate in equilibrium domain [1/d]
k_d	0.012603	1/d	fix	= DT50 55 d	Sorption rate [1/d]
f_ne	0.5		fitted		Ratio of Kf_eq / Kf_neq
S_eq0(t=0)	0.9509089	μg/g	fix		Conc. in equilibrium sorbed phase at t=0 [mg/kg]
S_neq0(t=0)	0	μg/g	fix		Conc. in non-equilibrium sorbed phase at t=0 [mg/kg]
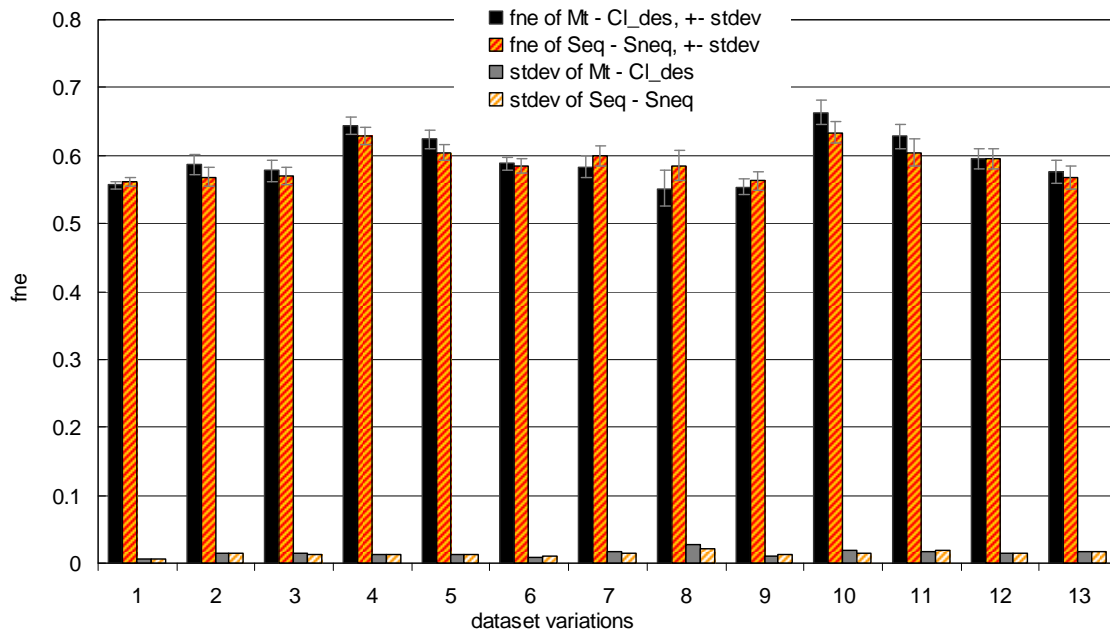
Figure A25-1. Estimated f_{ne} values and its standard deviations for 13 data sets, evaluated with two approaches (mean f_{ne} for data set creation was 0.6, with standard deviation of 0.06).

Table A25-3. Fitting results of 13 data sets using the M_{total} - $C_{l\,des}$ approach (mean f_{ne} for data set creation was 0.6, with standard deviation of 0.06).

Fit to M_{total} - Cl_des	estimated fne	standard deviation	95% probab. of T-test	coefficient of variation	chi2 error of Mt, %	chi2 error of Cl_des, %
1	0.55644	0.00584	6.81E-22	1.05%	0.21	0.56
2	0.58683	0.01570	1.73E-15	2.68%	0.67	1.10
3	0.57753	0.01567	1.67E-15	2.71%	0.72	0.84
4	0.64365	0.01220	4.07E-17	1.90%	0.43	1.10
5	0.62416	0.01349	1.80E-16	2.16%	0.53	1.04
6	0.58790	0.00942	8.61E-19	1.60%	0.33	0.91
7	0.58300	0.01615	2.62E-15	2.77%	0.71	1.01
8	0.55178	0.02690	4.54E-12	4.87%	1.24	1.55
9	0.55341	0.01144	1.55E-17	2.07%	0.29	1.38
10	0.66378	0.01867	2.22E-14	2.81%	0.73	1.35
11	0.62839	0.01793	1.22E-14	2.85%	0.61	1.71
12	0.59496	0.01516	1.03E-15	2.55%	0.61	1.19
13	0.57661	0.01666	4.12E-15	2.89%	0.68	1.30
arith. mean	0.59450	0.01418		2.39%		
median	**0.58683**	**0.01567**		**2.68%**		

Table A25-4. Fitting results of 13 data sets using the S_{eq} - S_{neq} approach
**(mean f_{ne} for data set creation was 0.6, with standard deviation of 0.06).**

| Fit to S_eq - S_neq	estimated fne	standard deviation	95% probab. of T-test	coefficient of variation	chi2 error of S_eq, %	chi2 error of S_neq, %
1	0.56182	0.00619	1.63E-21	1.10%	0.46	3.19
2	0.56861	0.01417	3.75E-16	2.49%	0.87	7.61
3	0.56946	0.01287	8.99E-17	2.26%	0.72	7.06
4	0.62977	0.01295	9.93E-17	2.06%	0.88	5.94
5	0.60429	0.01197	3.07E-17	1.98%	0.73	6.01
6	0.58419	0.01051	4.44E-18	1.80%	0.79	5.11
7	0.59978	0.01463	6.04E-16	2.44%	0.83	7.63
8	0.58565	0.02200	2.46E-13	3.76%	1.08	12.19
9	0.56283	0.01366	2.20E-16	2.43%	1.15	6.56
10	0.63390	0.01563	1.61E-15	2.47%	0.84	7.57
11	0.60436	0.01962	4.59E-14	3.25%	1.36	9.37
12	0.59588	0.01480	7.17E-16	2.48%	1.04	7.18
13	0.56787	0.01696	5.39E-15	2.99%	1.15	8.87
arith. mean	0.58988	0.01374		2.33%		
median	**0.58565**	**0.01417**		**2.44%**		
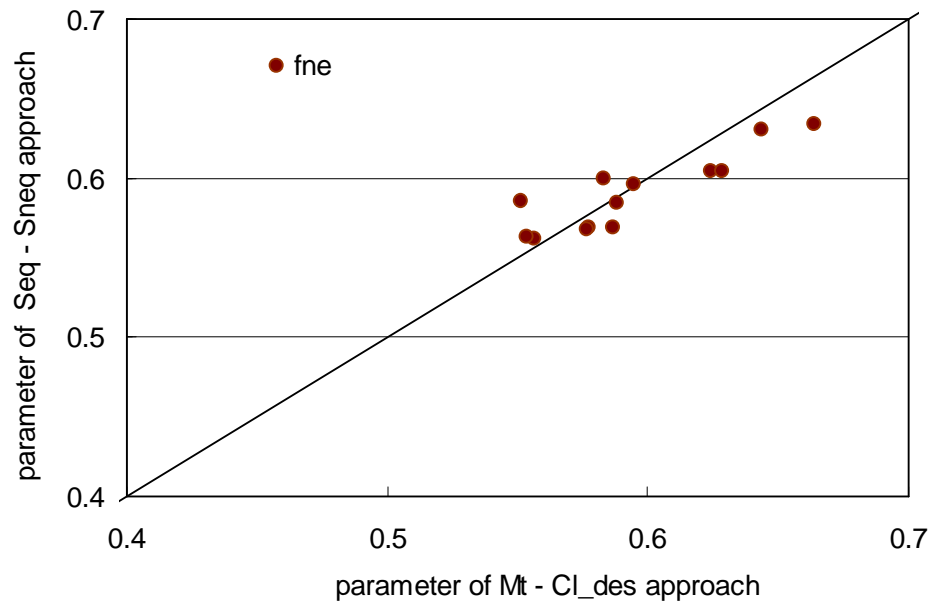
Figure A25-2. Estimated f_{ne} values for 13 data sets, directly compared for both approaches
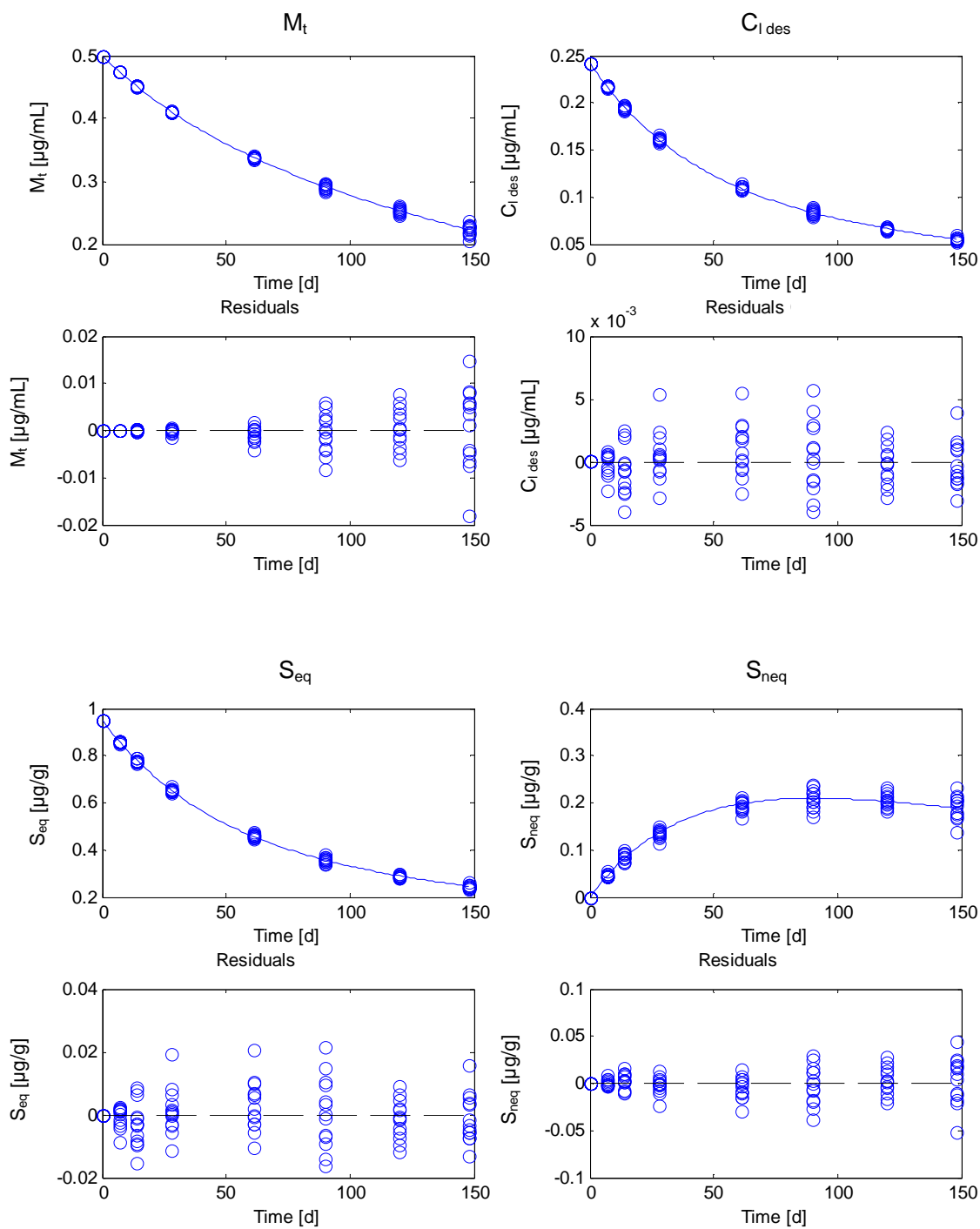**(mean f_{ne} for data set creation was 0.6)**
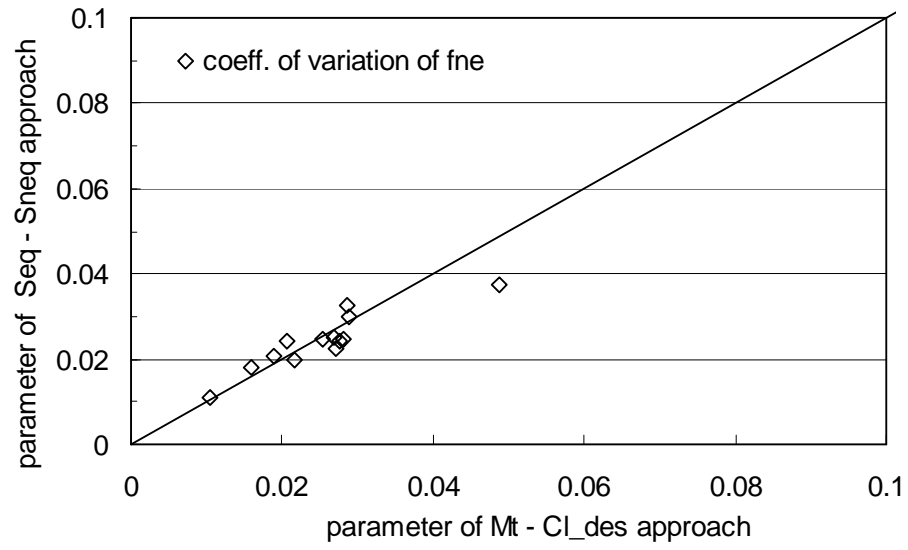
Figure A25-3. Coefficients of variation of estimated f_{ne} values for 13 data sets, directly compared for both approaches (mean f_{ne} for data set creation was 0.6).
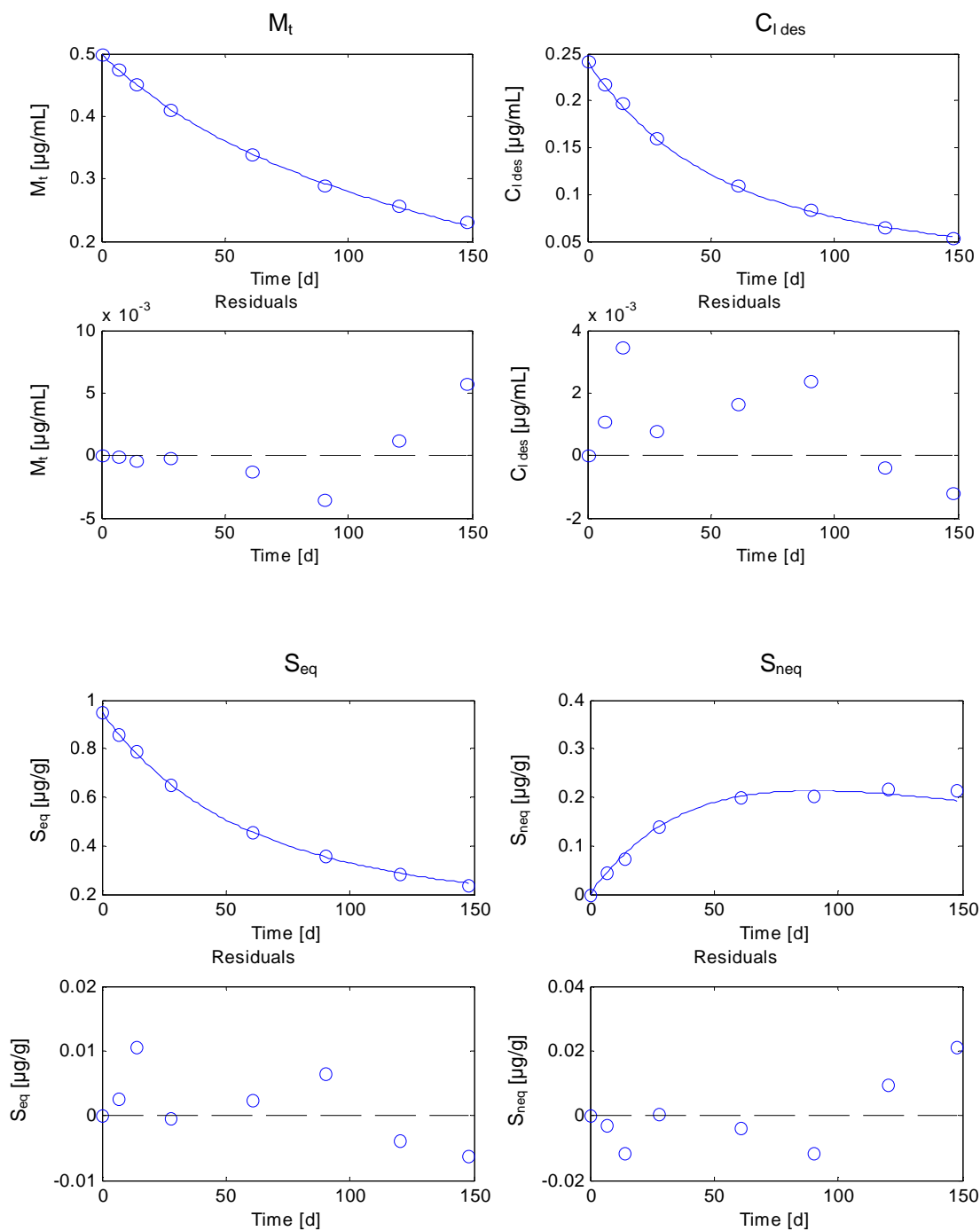
Figure A25-4. Visual fits of both approaches for data set 5.
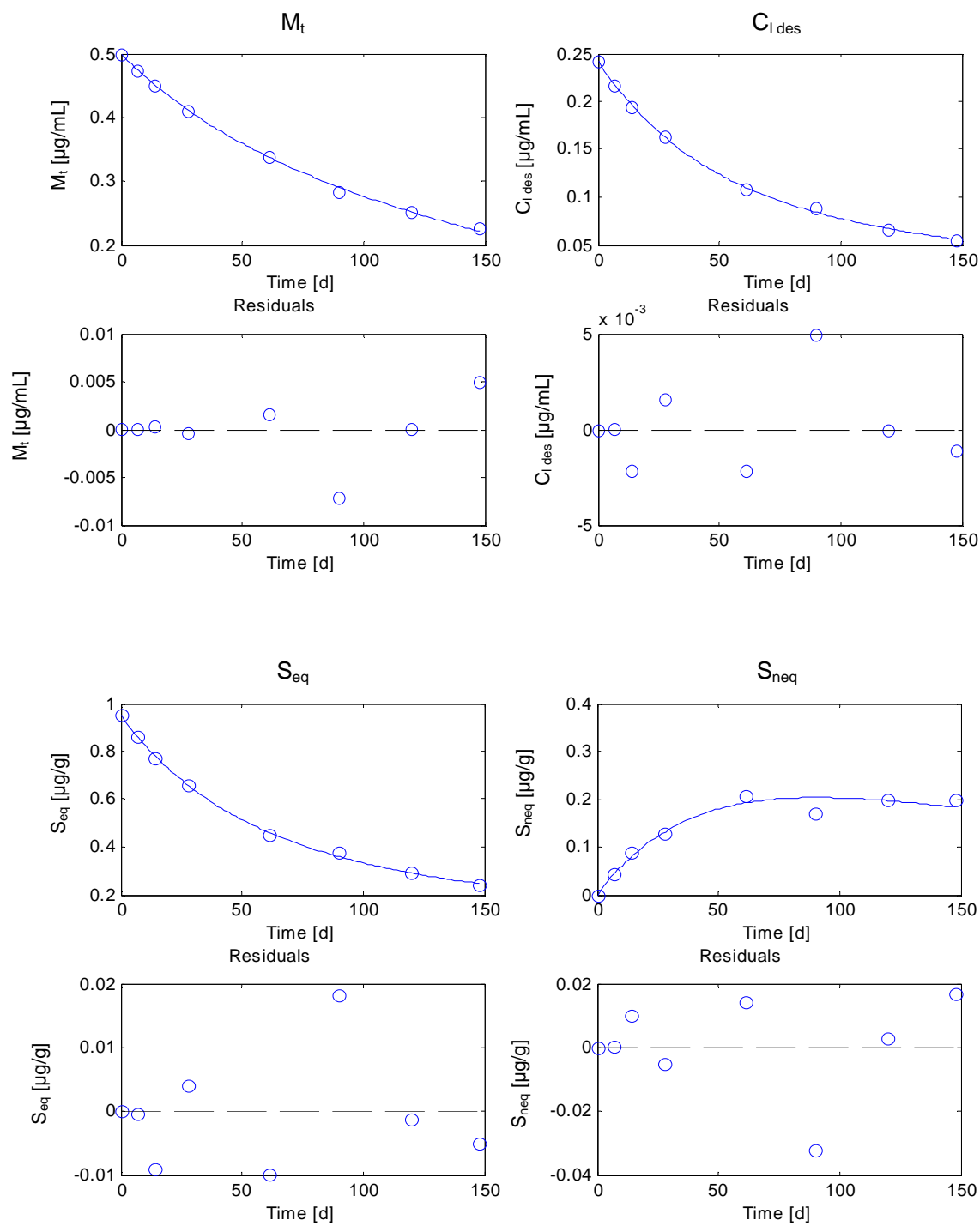
Figure A25-5. Visual fits of both approaches for data set 13.

Figure A25-6. Visual fits of both approaches for all data sets.

The compilation of the results provided in Tables A25-3 and A25-4 includes measures of the goodness of fit (χ^2 error). Obviously, the fit of S_{neq} results in higher χ^2 errors than the fits to the other variables, e.g. S_{eq}. This can be explained as a combined, systematic effect of the higher model error due to the higher sensitivity d S_{neq} /d f_{ne} compared to d S_{eq} /d f_{ne} and the lower mean S_{neq} compared to the mean S_{eq}. Note, that χ^2 is defined as the ratio between model error and the mean observed.

Conclusions

Both object functions, M_{total} - $C_{l\ des}$ and S_{eq} - S_{neq}, produce on average the same parameter estimates of 0.595 and 0.590, respectively which are very close to the "true value" of 0.6. No systematic differences were observed, either for the estimated value of the parameter or for its standard deviation. Thus the estimates of both approaches can be considered independent. As a result both object functions are fully equivalent.

References

MatLab. 2007. MatLab Version 7.4.0.287 (R2007a), Optimisation Toolbox, Statistics Toolbox, MatLab Compiler. The MathWorks Inc., USA. www.mathworks.com