RIVM report 601506 007/2001

Evaluation of pesticide leaching in lysimeter and field studies.
Parent substances.

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This investigation has been performed by order and for the account of the Directorate General for Environmental Protection, Directorate for Soil, Water and Agriculture, within the framework of project 601506, Consultancy on risk assessment for pesticides and biocides.

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Uw referentie :
Onderwerp : Erratum for RIVM report 601506 007/2001

In the RIVM report entitled:"Evaluation of pesticide leaching in lysimeter and field studies. Parent substances" an error occurred in chapter 3.3.2 at page 22 in the 6th sentence of the 4th paragraph.

'high' should be replaced by 'low'

You are informed about this error in order to prevent any misunderstanding in the application of the evaluation method described in the report.

Yours faithfully,

dr. W.H. Könemann (director)
Centre for Substances and Risk Asssessment

Bilthoven :8 juli 2002
Ons kenmerk :
Uw referentie :
Onderwerp : Erratum bij rapport 601506 007/2001

In het RIVM-rapport 601506 007, getiteld: 'Evaluation of pesticide leaching in lysimeter and field studies. Parent substances.' is helaas een fout opgetreden in hoofdstuk 3.3.2 op pagina 22 in de 6e regel van de 4e alinea.

'high' moet worden vervangen door 'low'.

U wordt geïnformeerd over deze fout om misverstanden bij de toepassing van de evaluatiemethode die in dit rapport wordt beschreven te voorkomen.

Hoogachtend,

dr. W.H. Könemann
hoofd van Centrum voor Stoffen en Risicobeoordeling

Acknowledgement

The Working group for the “Revision of the decision tree leaching” thanks the Steering Committee, consisting of delegates of the Ministry of Housing, Spatial Planning and the Environment, Nefyto, VEWIN, BASF, Bayer, and Syngenta Crop Protection for fruitful discussions at the start of the project and one year later. Based on their expertise and/or position dr. J.W. Tas, mr. M. van Assen, L. Joosten, ir. J.R. van de Veen, ir. S. van Nierop, ir. J. Henken are members of the Steering Committee.
The Working group for the “Revision of the decision tree leaching” likes to acknowledge Ir. Ing. W.W.M. Brouwer from the Plant Protection Service in Wageningen, for his constructive contribution to discussions about interpretation of pesticide leaching from lysimeter studies, as a former member of the working group .
Igor Dubus from the Soil Survey and Land Research Centre, Silsoe (UK) is kindly acknowledged for reviewing appendix 3, “Recommendations for calibrating the water balance of lysimeter studies with PEARL”.

Abstract

The first tier of the evaluation of pesticide leaching from soil is based on laboratory experiments and a computer simulation for a standard scenario. As higher tier experiments, lysimeter and field studies provide additional information on the leaching of pesticides from soil to groundwater. There is adequate guidance on how lysimeter and field experiments should be performed, but the way they should be interpreted is still subject of discussion and confusion. A group of experts from various institutes (RIVM, Alterra, CTB) have provided guidance for interpreting lysimeter and field experiments. The report documenting this guidance starts with recommendations for summarising lysimeter, field and simulation studies in a more consistent and objective way. Expert judgement has been converted in the best possible way to quantitative rules for evaluation. The lysimeter or field study is computer-simulated as well as possible, and the result is compared with measured leaching. The relative difference, here defined as the simulation error, is considered to be the endpoint of the evaluation of lysimeter or field studies. The simulation error will be used to correct the pesticide leaching computed for a scenario relevant to the registration of the pesticide. Some of the basis assumptions for calculation of the simulation error from lysimeter or field studies, in the absence of site specific information (DT50 and Kom), are only valid for parent substances. For the calculation of the simulation error of leached metabolites additional research is necessary, in order to define the correct assumptions for DT50 and Kom when site-specific data is missing.

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Samenvatting

Veld- en lysimeter studies leveren additionele informatie met betrekking tot de uitspoeling van bestrijdingsmiddelen naar het grondwater. Ze worden gebruikt als "higher tier" instrument, ná eerdere risico-beoordelingen die op laboratorium-experimenten en standaard simulaties zijn gebaseerd. Hoewel er voldoende richtlijnen zijn voor de uitvoering van dergelijke experimenten, is er vaak verwarring en discussie over de manier waarop veld- en lysimeterstudies moeten worden geïnterpreteerd met het oog op de toelating van bestrijdingsmiddelen. In dit rapport zijn richtlijnen voorgesteld in een nationale werkgroep voor de interpretatie van veld- en lysimeter studies uiteengezet, om te beginnen met aanbevelingen voor goede samenvattingen, zodat ze de informatie bevatten die essentiëel is voor de interpretatie van veld- en lysimeterstudies.
Kernpunt bij de interpretatie van veld- en lysimeterstudies is dat ze worden gesimuleerd met een uitspoelingsmodel (bv. PEARL). De verhouding tussen de berekende en de gemeten uitspoeling wordt de simulatiefout genoemd. De simulatiefout wordt gebruikt als correctiefactor op de uitspoeling, zoals die wordt berekend voor een scenario dat voor de registratie relevant is.
Voor een goede simulatie is het gebruik van locatie-specifieke invoerparameters van groot belang. Indien studies deze locatie-specifieke informatie niet verschaffen, zullen aannames worden gedaan die een conservatieve uitwerking hebben op de simulatiefout. Indien locatie-specifieke halfwaardetijden (DT50) en adsorptiecoëfficienten (Kom) ontbreken, moet worden gerekend met de laagste DT50 en de hoogste Kom uit de waarden in het bestrijdingsmiddel-dossier.
De simulatiefout wordt voor veld- en lysimeterstudies op verschillende wijzen berekend.

Voor **lysimeterstudies** geldt:

$$E_{SIM} = \frac{C_{lys}}{M_{lys}}$$

E_{SIM} is de simulatiefout
M_{lys} is gemeten cumulatieve uitspoeling
C_{lys} is berekende cumulatieve uitspoeling

en voor **veldstudies** geldt:

$$E_{SIM} = \prod_{i=1}^{n} \frac{C_i}{M_i}$$

E_{SIM} is de simulatiefout
M_i is gemeten concentratie in het bovenste grondwater op tijdstip i
C_i is berekende concentratie in het bovenste grondwater op tijdstip i
n is het aantal monstername tijdstippen

In beide gevallen wordt de gehele studieperiode in beschouwing genomen. Omdat het voor veldstudies niet mogelijk is de cumulatieve uitspoeling te bepalen, wordt daar op elk relevant monstername tijdstip de simulatiefout berekend op basis van concentraties in het bovenste grondwater. Het geometrisch gemiddelde van alle monsternametijdstippen geldt als de simulatiefout van het veldexperiment. Voor metingen beneden de detectielimiet wordt de concentratie gelijk gesteld aan de detectielimiet. De simulatiefout wordt dan weergegeven met een < teken. Als de berekende waarde 0,000 µg/l is, wordt er gerekend met C<0,001 en de simulatiefout wordt dan weergegeven met een > teken. Punten waarbij de berekende waarde <0,001 µg/l is èn de gemeten waarde beneden de detectielimiet ligt worden bij de berekening van de simulatiefout buiten beschouwing gelaten.

Executive summary

Lysimeter and field studies provide additional information with respect to the leaching of pesticides to the groundwater. They are used as higher tier information, after prior assessments based on laboratory experiments and standard simulations. Although there is a number of guidelines for the performance of field or lysimeter studies, confusion and discussion exists on the interpretation of the results in the framework of the pesticide registration. In this report guidance for the interpretation of field and lysimeter studies is given, starting with recommendations for summaries, so that they will contain all the essential information for the interpretation of field and lysimeter studies.
The crux in the interpretation of field and lysimeter studis is that they are simulated with a leaching model (i.e. PEARL). The ratio between calculated and measured leaching is called the simulation error. The simulation error is used as a correction factor for the simulated leaching in a scenario relevant for the registration.
For a proper simulation the use of location-specific parameters is essential. When studies do not provide this location-specific information, assumptions will be made with a conservative effect on the simulation error. In the absence of location-specific information the lowest DT50 and the highest Kom from the pesticide dossier will be taken as input for the simulations. The calculation of the simulation error is slightly different for field and lysimeter studies.

Used for **lysimeter studies**:

$$E_{SIM} = \frac{C_{lys}}{M_{lys}}$$

E_{SIM} is the simulation error
M_{lys} is measured cumulative leaching
C_{lys} is calculated cumulative leaching

Used for **field studies**:

$$E_{SIM} = \prod_{i=1}^{n} \frac{C_i}{M_i}$$

E_{SIM} is the simulation error
M_i is the measured concentratiion in the upper groundwater at time i
C_i is the calculated concentration in the upper groundwater at time i
n is the number of samples

In both cases the whole study period is considered. In field studies it is not possible to determine the cumulative leaching, so the ratio is calculated based on the concentration in the upper groundwater at individual time points. The geometrical mean of all individual ratios is taken as the simulation error of a field experiment. For measurements below the detection limit the values of the detection limit will be used, and the simulation error gets a >sign. Computed values of 0.000 µg/l, will be treated as <0.001 µg/l and the simulation error also get a < sign. Time points where the calculated leaching is <0.001 µg/l ànd the measured concentration is below the detection limit are not used for the calculation of the simulation error.

1. Introduction

The estimation of the risk of groundwater contamination by pesticides is a major task of the registration authorities. Before pesticides can be marketed they have to be registered, which can only be done if they comply with legal criteria. To protect the groundwater, there must be **reasonable certainty** that the concentration of the pesticide in the groundwater at 10 m depth does not exceed 0.1 μg/l. It should be noted that the criterion of 10 m depth is the Dutch elaboration of the European standard. Underlying assumptions are that pesticides are used according to Good Agricultural Practice and that downward transport is a normal chromatographic process. It seems to be simple, but in many cases it turns out to be hard to obtain enough certainty that a pesticide satisfies the groundwater criterion. There are many uncertainties in the assessment of the leaching risk. Uncertainties of **not knowing** the actual values of pesticide properties, but also uncertainties in the sense of **variability** of e.g. soil and climatic conditions in space and time.
In order to streamline decisionmaking, a decision tree is used to check whether a pesticide can be considered to be safe with respect to groundwater (CTB, 1999). The first tier screening is performed with average half-life time (DT50) and average adsorption-coefficient (Kom), based on laboratory experiments. These data are used in a model calculation (USES), to estimate the leaching for a standard situation (soil, crop, weather). USES utilizes a meta-model version of PEARL (USES, 2001). Guidance for the interpretation of laboratory experiments is available (Brouwer *et al.*, 1994).
At present, in the Netherlands, authorisation can be granted in tier 1 with respect to groundwater contamination if the active substance and relevant metabolites show a leaching less than 0.001 μg/l to the upper groundwater (1-2 m deep). The trigger value 0.001 μg/l is the result of dividing the legal criterion by a safety factor of 100. Reasonable certainty in this **first tier** is obtained by the introduction of this factor 100. It accounts for uncertainty and variability of the major input-parameters DT50 en Kom and for the simulation error. Currently, the Working Group for Revision of the Decision Tree on Leaching is occupied with specifying and quantifying the term reasonable certainty, and is reconsidering the safety factor.
If the estimated concentration in the upper groundwater exceeds the trigger value in tier 1, additional information should be provided to ascertain that leaching does not exceed 0.1 μg/l. In **tier 2** lysimeter or field experiments in combination with calculations can provide enough evidence. Lysimeter or field studies could also be asked for by the authorities if minor metabolites are found to leach from aged residue leaching experiments or if monitoring data show the presence of the pesticide or its metabolites in the groundwater, in contrast with model predictions.
A lysimeter or field study has advantages over laboratory studies:

- a stronger resemblance to environmental conditions in the field soil;
- no significant disturbance of the soil;
- possibility to grow crops and to study the fate of pesticides in soil/plant systems;
- integration of processes (transformation and leaching) that are measured separately in the laboratory.

Some advantages of lysimeter studies over field studies are:

- the fate of radiolabelled compounds can be measured;
- processes of water and solute transport can be studied separately.

Some advantages of field studies over lysimeter studies are:
- no edge effects or oasis effects;
- the soil profile can be sampled at intervals;
- the behaviour of the residues in the groundwater zone can be followed.

There is international agreement on how a lysimeter experiment should be performed (CTB, 1999; OECD, 2000; BBA, 1990). However, there is no official guidance for the interpretation of the results. Interpretation is necessary because, despite the advantages described above, the results of different studies are more difficult to compare (a.o. because of lack of control over environmental parameters). The results reflect time and location of the study, and it is difficult to extrapolate the results to other situations. Because lysimeter studies are very expensive and time-consuming, it is desirable to have a method to generalise the results. Van de Veen and Boesten (1996) initiated a method for standardisation of the pesticide concentration in the lysimeter leachate to a vulnerable scenario. In this report the method is being developed and specified further.
On request of the CTB (Board for the Authorisation of Pesticides) this report deals with the following questions:
- How should lysimeter studies be interpreted in the framework of pesticide registration in the Netherlands?
- How can expert judgements of lysimeter studies be made more transparent and reproducible?
- How to deal with various studies with different results and different qualities?

The working group for the revision of the decision tree leaching was created to tackle these questions. Members were chosen from governmental institutes involved in the research of pesticide leaching (RIVM , Alterra, the Plant Protection Service and the CTB), because of their expertise in interpretation and assessment of higher tier leaching studies. The direct participation of the Plant Protection Service was later on changed. However, they were kept informed through agendas of planned meetings, minutes and discussion memos and draft versions. The final draft was approved for publication by the Plant Protection Service.

The goals and progress have been discussed with a Steering Committee, consisting of representatives of the Ministry of Housing, Spatial Planning and the Environment, pesticide manufacturers (Nefyto, BASF, Bayer, Syngenta Crop Protection) and the drinking water companies (VEWIN).

Because there are a lot of similarities in the interpretation of field and lysimeter studies, the report also covers the interpretation of field experiments. The answers to the questions are given in chapter 2 with the description of the contents of a good summary and the assignment of a quality index and in chapter 3 with guidance for an objective interpretation of a lysimeter or field study.

2. Summarising lysimeter and field studies

2.1 Introduction

The report of a field or lysimeter study follows a pathway along evaluating expert, advisory panel and decision-maker. Usually the evaluating expert summarises the report on which the decision is primarily based. To guarantee consistent decisions based on the same principles and criteria, the summary must be **objective**, not affected by the industry's interpretation nor affected by the preferences of the person who made the summary.
First of all the **quality** of the lysimeter or field study must be determined and remarks should be made in the summary to explain reasons for a possible lower quality. The use and interpretation of the study depend on its quality. For instance, information gaps could be filled-in by worst-case assumptions or even lead to rejection of the lysimeter study. Moreover a summary must be **suitable** to make a proper independent evaluation possible. Therefore it must contain all the essential information (see §2.3) to reach a reasonable understanding of the vulnerability of the lysimeter or field situation, as compared to a scenario relevant for the registration of the pesticide, and to allow for a rough extrapolation of the leaching result to other situations.

2.2 Quality of a lysimeter or field study

The quality of a lysimeter study is a measure of the reliability and the completeness of the study. Lysimeter and field studies are performed for the greater part under natural conditions. The resemblance of the conditions with a situation relevant for the Dutch registration is not a criterion for the intrinsic quality of the study, neither is the usefulness of the result.
Assigning a quality index to study reports when they are summarised, is part of the quality procedure at RIVM-CSR. The general methodology is described in the RIVM-report of Mensink *et al.* (1995).
The quality of a study can be determined by answering the following questions:

- Was the layout and experimental set-up adequate?
- Was the soil free of pesticide use in the previous years?
- Was agricultural management in accordance with GAP?
- Are nominal and actual application rates relevant for the intended use of the pesticide?
- Have all the relevant conditions and results been reported? (See next paragraph)
- Is the method of sampling and analysis valid?
- Is de sampling scheme adequate?
- Is the analytical recovery satisfactory and the limit of quantification relevant for the residues?

Three quality classes are distinguished:
Q1: study is complete, verifiable and reliable and contains all the information needed for interpretation of the results.
Q2: study does not meet all the requirements, but the most essential data are present.
Q3: Essential information is missing or improper methods have been used. The results can not be interpreted.

The next paragraph lists all the items that should be addressed in the summary. Consequences of missing data or of not meeting the requirements for the quality index are mentioned in the last column.

2.3 Contents of a summary

Table 1 and Table 2 give checklists for all the items that should be described in the summary. The tables do not provide guidance for the performance of a lysimeter or field study. Guidance for the performance of lysimeter/field tests is available elsewhere (CTB, 1999; OECD, 2000; BBA, 1990). In one column indications for the quality of the study can be given. If one essential item receives a Q3, then the whole study will be assigned Q3. However there are many items, which can have a lower quality, without loosing the possibility for interpretation. These items are indicated with Y. If one item receives a Y, then the whole study will be assigned Q2. If there are several items receiving a Y, it is possible to assign a Q3 to the study as whole, because when there are too many uncertainties, the study as a whole is not reliable enough for interpretation.

Table 1 Checklist for the summary of a lysimeter study

	Items	Notes	Reliability lower?[1]
DESCRIPTION	**GLP**	Y/N	
	Guideline	e.g. BBA IV-3	
	Location of experiment	Near-by place, county/province/state and country	
	Duration of experiment	Until reasonable certainty on the leaching behaviour of the test substance is obtained. Test duration must be long enough to measure possible breakthrough of the pesticide	E
	Soil type/texture	According to USDA; soil relatively sensitive to leaching is preferred	Y
	Origin	Near-by place, county/province/state and country	
	%OM or %OC	In each layer	Q3
	pH	In each layer, describe method e.g. pH(KCl), pH(H_2O) or pH($CaCl_2$); molarity For parent compounds or metabolites that show pH dependent sorption, the pH for different soil layers is essential. If not reported for pesticides with pKa between 3 and 10 then Q=3.	E
	CEC	Essential for compounds showing cation exchange	
	Soil history	Pesticides used and crops grown in the last 3 years. The use of the pesticide under consideration or structural analogues in previous years will result in a lower quality (Y)	E
	Parallel laboratory DT50/Kom	Kom and DT50 at 20°C in the lysimeter soil for plough layer and deeper layers if available.	Y
	Lysimeter	Monolith in inert casing, layout of facility	Y
	Number of replicates	≥2	Y
	Dimensions	Depth ± 1m, area ≥0.1 m^2 for cereals and fallow, ≥0.25 m^2 for other crops	Y
	Treatment	Repeated application only in compliance with GAP	E
	Formulation	Active ingredients and adjuvents or impurities	
	Label	Uniform or in the most persistent part of the molecule, radiochemical purity	E
	Application rate	Kg/ha, nominal and actual	Q3
	Application scheme	Exact application dates	Q3
	Application method	i.e. spray, soil injection, seed treatment, growth stage crop	E
	Untreated control	Y/N	
	Agricultural practice	Describe the crops grown, including dates of sowing, emergence and Harvest, other pesticides used, nutrients applied, soil cultivation, also in the direct surroundings (1m) of the lysimeter	Y
	Analytical method	Methods of extraction and analysis, recovery, limit of detection. Reference compounds	Q3
	Leachate	Specify sampling dates, or intervals	
	Soil	N samples, in layers of ...-... cm, ...-... cm and ...-... cm, Sampling of the plough layer is only allowed immediately before a soil tillage operation and after termination of the experiment. Total radioactivity, extractable radioactivity, bound residues, individual compounds and moisture content should be analysed.	E Q3
	Crop	What parts of the plants are analysed?	

Table 1 continued. Checklist for the summary of a lysimeter study

	Items	Notes	Reliability lower?[1]
RESULTS	**Temperature**	Average annual air temperature measured at a nearby weather station (<25 km, average annual soil temperature at 10 cm depth)	
	Precipitation	Annual and total precipitation on-site, extreme events	E
	Irrigation	n times, ... mm/event, total amount. Irrigation is allowed when necessary for crop growth or to adjust the actual precipitation to long-term average, but not more than 20 mm/day.	E
	Leachate	Annual amount and total amount of water. Check whether the amount of percolate does reflect normal hydrological conditions. For each year: number of observations , range, average concentration for the a.i. and the metabolites Accumulated leaching	E
	Soil	Bound residue (sum of all layers) as ...% of a.r. Extractable radioactivity (total and for each individual layer) as ...% of a.r.	
	Crop	X% of a.r. was found in crops	
	Mass balance	...% of applied radioactivity leached, ...% of applied radioactivity in soil layers for parent compound and metabolites	
REMARKS	**Remarks** **Recalculations**	Give reasons for assigning a quality index 2 or 3 If not given or miscalculated by the author, recalculate the accumulated leaching (kg) of the pesticide and its metabolites	

[1] E=expert judgement, Y=reliability is lower and Q≠1 if item is not reported or is not according to guidance, Q3 is given when this item is not reported.

Table 2 Checklist for the summary of a field study

	Items	Notes	Reliability lower?[1]
DESCRIPTION	**GLP**	Y/N	
	Guideline	e.g. CTB (1999)	
	Location of experiment	Near-by place, county/province/state and country	
	Duration of experiment	Until reasonable certainty on the leaching behaviour of the test substance is obtained. Test duration must be long enough to measure possible breakthrough of the pesticide	E
	Soil type/texture	According to USDA; soil relatively sensitive to leaching is preferred	Y
	%OM or %OC	In each layer	Q3
	pH	In each layer, describe method e.g. pH(KCl), pH(H_2O) or pH($CaCl_2$); molarity For parent compounds or metabolites that show pH dependent sorption, the pH for different soil layers is essential. If not reported for pesticides with pKa between 3 and 10 then Q=3.	E
	CEC	Essential for compounds showing cation exchange	
	Soil history	Pesticides used and crops grown in the last 3 years. The use of the pesticide under consideration or structural analogues in previous years will result in a lower quality (Y)	E
	Parallel laboratory DT50/Kom	Laboratory Kom and DT50 at 20°C in the soil , for plough layer and deeper layers if available	Y
	Field plot	Layout of facility, vicinity of buildings, surrounding areaand crops, slope, depth of groundwater table, direction of groundwater flow	Y
	Number of replicates	≥2 plots and control plot	Y
	Dimensions	Preferably >100m^2/plot	Y
	Treatment	Repeated application only in compliance with GAP	E
	Formulation		
	Application rate	Kg/ha, nominal and actual	Q3
	Application scheme	Exact application dates	Q3
	Application method	i.e. spray, soil injection, seed treatment, growth stage crop	
	Untreated control	Y/N	
	Agricultural practice	Describe the crops grown, including dates of sowing, emergence and harvest, other pesticides used, nutrients applied, soil cultivation	Y
	Analytical method	Methods of extraction and analysis, recovery, limit of detection. Reference compounds.	Q3
	Groundwater	Specify sampling dates, or intervals. Position (depth) of sampling tubes, method of groundwater sampling.	
	Soil	n samples, in layers of ...-... cm, ...-... cm and ...-... cm,	E

Table 2 continued. Checklist for the summary of a field study

	Items	Notes	Reliability lower?[1]
RESULTS	**Temperature**	Average annual air temperature measured at a nearby weather station (<25 km, average annual soil temperature at 10 cm depth)	
	Precipitation	Annual and total precipitation on-site, extreme events	E
	Irrigation	n times, ... mm/event, total amount. Irrigation is allowed when necessary for crop growth or to adjust the actual precipitation to long-term average, but not more than 20 mm/day.	E
	Groundwater	Per sampling time: number of observations , range, average concentration for the a.i. and the metabolites.	E
	Soil	Extractable residue of relevant compounds (total and for each individual layer)	
REMARKS	**Remarks** **Recalculations**	Give reasons for assigning a quality index 2 or 3 If not given or miscalculated by the author, recalculate the average field concentration per sampling time (μg/L) of the pesticide and its metabolites	

[1] E=expert judgement, Y=reliability is lower and Q≠1 if item is not reported or is not according to guidance, Q3 is given when this item is not reported.

3. Interpretation of lysimeter and field studies

3.1 The purpose of lysimeter and field studies

In the framework of a tiered risk evaluation, lysimeter or field studies should provide additional information on the risk of leaching. This means that a lysimeter study should show whether or not leaching of the pesticide and its metabolites exceeds 0.1 μg/l in the upper groundwater.
A lysimeter or field study can decrease the uncertainty of an earlier assessment (tier 1) by confirming that the risk of leaching is low (C_{leach} <0.1 μg/l). On the other hand it can disprove the prior assessment by showing that more realistic conditions and parameters yield a different evaluation result.
Lysimeter or field studies are performed for the greater part under natural conditions. This gives information in addition to that in tier 1, because more processes and interactions are reflected. However it also implies that conditions are variable and that they cannot be controlled. Generally, the experimental conditions deviate from the conditions relevant for a Dutch registration (target scenario). So, the leaching measured in a lysimeter or field study cannot be used directly, but it has to be extrapolated to conditions relevant for the intended use.
In principle, a computer simulation model can be used to translate the results of lysimeter or field studies. This is done by comparing computed and measured leaching. The ratio between the lysimeter/field computations and the lysimeter/field measurements will be used as a correction for the leaching calculated for a relevant Dutch scenario. This ratio is called the simulation error, which is an **endpoint** of tier 2 lysimeter/field studies. If the simulation error = 1 the model describes the measured leaching perfectly. If the simulation error >1, this means that the simulation model overestimates leaching.

Similar to building a database of DT50 and Kom values in tier 1, a database of simulation errors can be built, enabling the transparent and reproducible use of information from all the lysimeter/field experiments. The whole procedure is illustrated in figure 1.

Definitions

Simulation error = the ratio between computed and measured leaching for the same scenario (lysimeter or field) due to processes not properly described by the model, or due to unrealistic model input.

Target scenario = scenario relevant for the registration of the pesticide in the Netherlands.

Adjusted estimate = computed leaching in a target scenario that has been corrected by the simulation error (formerly known as standardised leaching.)

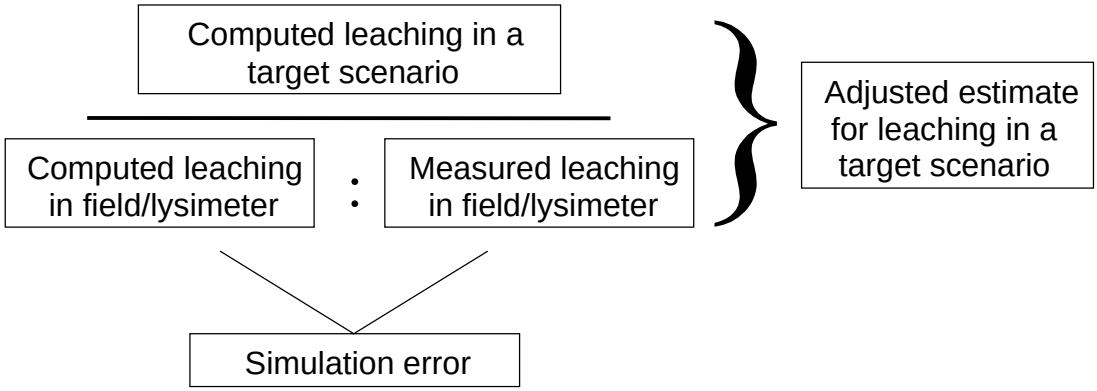

Figure 1 Procedure of lysimeter/field study interpretation

3.2 Relevance and usefulness of lysimeter and field studies

The resemblance of the experimental conditions in the lysimeter/field to those in a relevant Dutch use situation is not a criterion for the quality of the study (as classified in the summary). The same holds for the usefulness of the result.

The relevance of the experimental conditions for the Dutch use situation is not questionable if all the essential information is available to extrapolate the results. Then, lysimeter/field studies can be extrapolated to a relevant Dutch use scenario. The so-called adjusted estimate will be compared with the legal criterion of 0.1 µg/l in the upper groundwater.

An evaluation problem arises when leaching is below the limit of quantification, for example <0.01 µg/l. These outcomes are not always useful. There are some possibilities why this may occur:

- The lysimeter/field experiment was performed without being triggered by tier 1. In this case the lysimeter/field study was not necessary, so it is not considered relevant. No effort needs to be made to extrapolate the result. However, the lysimeter/field study is useful because it confirms the prior assessment and thereby reduces the uncertainty of the risk assessment.
- The lysimeter/field experiment was triggered by tier 1, but the experimental conditions are not vulnerable enough. In guidelines for the performance of lysimeter/field studies it is mentioned that a vulnerable soil profile must be used in the experiment. Other scenario influences such as precipitation and temperature could be more favourable for low water percolation or faster biodegradation or higher evaporation, resulting in a less vulnerable scenario. In that case the lysimeter/field study may be not useful.
- The lysimeter/field experiment was triggered by tier 1, but other processes than included in the tier 1 assessment lead to lower leaching levels (e.g. photodegradation on the soil surface)
- The lysimeter experiment was triggered, and the scenario was realistic worst case with respect to leaching. Still, leaching was lower (<LOQ) than expected in tier 1. A parallel laboratory experiment with the lysimeter soil shows whether the soil has a high transformation potential for the pesticide, resulting in a lower DT50. Such a parallel laboratory experiment is thus essential for a proper simulation of the lysimeter experiment.

If the lysimeter or field experiment was triggered by a slight exceedence of 0.001 µg/l in the tier 1 assessment, it can be expected that leaching will not be observed in the lysimeter or field experiment when the limit of quantification is 0.01 µg/l. If the lysimeter or field study has an expected equal or

higher vulnerability than the relevant Dutch scenario the fact that no leaching was observed should be accepted as such. Possible criteria for the evaluation of lysimeter/field study vulnerability are given in Table 3.

Table 3 Vulnerability checklist. Default values (in PEARL) for the Dutch situation are given. Data in the column "Dutch target scenario"are given as an example. Data in target scenario may differ somewhat due to the proposed use of the substance.

Item	**Lysimeter/field**		**Dutch** target scenario	Lysimeter more vulnerable?
	1st year	2nd year		
average annual temperature (°C)			9.3°C	$T_{lys} < T_{Dutch}$ -0.5°C → yes $T_{lys} > T_{Dutch}$ + 0.5°C → no
precipitation (mm)			862	$P_{lys} < P_{Dutch}$-100 → no $P_{lys} > P_{Dutch}$+100 → yes
precipitation excess* (mm) *only in lysimeter studies			380	$E_{lys} < E_{Dutch}$-100 → no $E_{lys} > E_{Dutch}$+100 → yes
organic matter top layer (%) profile (%)			4.7 1.65	$OM_{Dutch} > OM_{lys}$ → yes
sand (%)			88	only relevant for very mobile compounds $S_{Dutch} > S_{lys}$ → no
pH			6.5	relevant for pH dependent sorption
time of application				autumn more vulnerable than spring
application rate				
replications				
crop(s)				difficult to compare but important to be aware of differences
DT50 (days) and Kom (l/kg)	from parallel experiment		average from dossier	$DT50_{lys} > DT50_{dossier}$ → yes $Kom_{lys} > Kom_{dossier}$ → no, or $(DT50/Kom)_{lys} < (DT50/Kom)_{dossier}$ → no

3.3 Calculation of the simulation error from lysimeter studies

The simulation error is defined as the ratio between computed and measured leaching for the same lysimeter/field scenario. Differences may occur due to processes not properly described by the model, or due to unrealistic model input. The equation is:

$$E_{SIM} = \frac{C_{lys}}{M_{lys}} \qquad \textbf{Equation 1}$$

E_{SIM} = simulation error
C_{lys} = computed leaching
M_{lys} = measured leaching

Leaching can be expressed in various terms, e.g. annual average concentration, maximum concentration, accumulated leaching. The simulation error could be calculated with any of these quantities, as long as the measured and the simulated concentration represent the same entity. Accumulated leaching is defined as the total mass of the pesticide (or its metabolite(s)) leached over the whole experimental period. In the simulation of pesticide leaching, accumulated leaching is a robust parameter and this quantity is also easily obtained from the measurements. It is therefore preferred to **use the accumulated leaching for the calculation of the simulation error in lysimeter studies**. In PEARL accumulated leaching is expressed as Areic Mass Leached (kg/ha).
The maximum concentration given in the PEARL output is not similar to the maximum concentration in the lysimeter leachate, because PEARL gives the concentration at a certain moment, whereas a leachate sample is collected over a certain time interval. So, the maximum concentration cannot be used for calculation of the simulation error.
For field studies the concentration measured at particular sampling times will be used for comparison with computed concentrations to calculate the simulation error. Accumulated leaching generally cannot be calculated from measurements in field studies.

3.3.1 Measured leaching

The leachate of a lysimeter is collected and the volume and the concentration are determined regularly (e.g. every two weeks in the wet season and every 1-2 months in the dry season). If accumulated leaching is not reported as such, it can be calculated with the following formula:

$$AAML = \sum_{i=1}^{n} V_i \cdot C_i \qquad \textbf{Equation 2}$$

$AAML$ =Accumulated Areaic Mass Leached (mg/m^2)
i = single leachate sample
n = number of leachate samples
V_i = areic volume of leachate sample (m^3/m^2)
C_i = concentration of pesticide in single leachate sample (mg/m^3)

Attention should be given to the unit in which the measured concentration is expressed. Radioactivity is a sum of the parent compound and its metabolites. If metabolites are involved check the units, distinguishing equivalents, mol or µg. In the comparison with computations, the units should match that used for the output in PEARL, which gives kg/ha (lysimeter studies) for the Areic Mass Leached. When the leaching in a lysimeter study was always below the limit of quantification, one should assess whether the lysimeter study was vulnerable enough to support a decision for the intended use scenario. If the lysimeter study is less vulnerable than the scenario of concern, then the study is considered to be not useful. If the lysimeter study represents a relatively vulnerable situation, zero leaching could be accepted without extrapolation. Possible criteria for the evaluation of lysimeter/field study vulnerability are given in Table 3.
Because relations in the leaching models are strongly non-linear it is impossible to decide whether one factor is neutralised by another. If the answer to any of the questions in Table 3 is **no**, then the **lysimeter** is potentially **less vulnerable** than the scenario of concern and the lysimeter study is considered to be **not useful**.

3.3.2 Simulated leaching

The Achilles' heel in the whole standardisation procedure may be the calculation of (accumulated) leaching from the lysimeter, which requires a lot of detailed input. In Table 4 the major requirements of a standardisation are given. Principles of Good Modelling Practice should be kept in mind (Travis, 1995). The basic goal of Good Modelling Practice is to assure transparent and reproducible modelling steps. **Appendix 2** sketches the outlines of Good Modelling Practice for model users.

Often, the water flow part of the leaching model must be calibrated to describe water flow correctly. In this procedure parameters affecting crop water uptake and evapotranspiration and in second instance soil evaporation parameters may be optimised to fit the outflow pattern and the total amount of percolation water. In **appendix 3** some recommendations for the optimisation of hydrological parameters are given. When calibration of the water balance has been successfully completed, simulation of the pesticide leaching can begin. The calibration of water flow has much influence on the calculation of pesticide leaching. This step in the whole evaluation of lysimeter and field studies is still not transparent and reproducible, because there is no guidance or a generally accepted method for the calibration of the hydrology. However, a detailed description of the calibration is essential.

The input for the simulation should resemble the lysimeter/field experiment as closely as possible. That means site-specific daily input of temperatures, precipitation and irrigation events. A good description of the soil profile is needed. Application method and applications times should match with the application intended for in the registration. Boundary conditions should be appropriate for the lysimeter. The input of a site-specific adsorption coefficient and a site-specific DT50 improve the quality of the simulation study.

In general, a reasonable worst case approach is followed when data are missing. For a conservative approach of the simulation error it implies that the simulated leaching must be relatively low. For parent substances, this is achieved by assuming a relatively low DT50 and a relatively high Kom in the lysimeter scenario. **The lowest DT50 and the highest Kom from the data in the dossier will be used for the simulation of leaching, when site-specific values are not available.** This will lead to a comparatively high simulation error, which is used for dividingthe accumulated leaching calculated for a relevant scenario.

The use of inverse modelling techniques for the derivation of site-specific DT50 and Kom from lysimeter and field studies is still under discussion (see **appendix 4**).
Because the applicants mostly have a lot of data available in digital form (data that are not always reported), it is most efficient that the applicant reports the simulation error. As a check-up method for evaluators, a rough extrapolation method is described in **appendix 5**.

Table 4 Checklist for simulation of lysimeter leaching

Item	Lysimeter simulation	Reliability lower?[1]
Soil profile	Lysimeter soil	Q3
no. of horizons	According to profile description	Y If profile doesn't show horizons, the profile must be characterised for each layerr of approx. 30 cm.
Depth	at least 1 m	E
OM in layers	Measured	Q3
pH	Measured	For compounds with pKa between 3 and 10 pH dependent sorption can be expected, therefore the pH is essential. If there is no pH given the mobility can not be interpreted →Q3
Meteo **Temperature** **Precipitation** **solar radiation**	At location daily min-max (°C) daily total (mm) measured or calculated	If daily temperatures and precipitation have not been used for the calculations but approximations based on average temperature and precipitation the outcome is indicative →Q3
Water balance[2]	calibrated amount and pattern of percolation	E. Deviation of 30 mm or 10% of the total amount of water percolated is acceptable.
Application scheme	As in lysimeter study	Y
Crop	As in lysimeter study	Input parameters of crop should match the crop grown in the lysimeter as good as possible. Estimations based on resemblance to another crops is allowed if the crop is not in the FOCUS database.
DT50	From parallel experiment	If the DT50 in the lysimeter soil has not been determined in a parallel experiment, the lowest DT50 from the dossier should be used
Kom	From parallel experiment	If the Kom in the lysimeter soil has not been determined it is acceptable to take the highest Kom from the dossier.
Duration of simulation	Duration of lysimeter experiment	It is suggested to include a warm-up period of 3 months or longer in the calculateions. Environmental conditions as observed prior to the experiment are recommended as input.

[1] E=expert judgement, Y=reliability is lower and Q≠1 if item is not reported or is not according to guidance, Q3 = given when this item is not reported.
[2] Guidance for the calibration procedure is given in appendix 2.

3.4 Calculation of the simulation error from field studies

In lysimeter studies it is recommended to simulate the accumulated mass leached, but in field studies the concentrations in the groundwater have to be used, because the amount of percolation water and consequently the accumulated leached amount can not be measured directly under field conditions. For the extrapolation of a field study, the simulation error will be calculated for each sampling time. The average of all the individual simulation errors will be derived and used for the risk evaluation.

The Dutch guideline for field studies (CTB, 1999) prescribes the following measurements of pesticide concentrations in the field:

- in groundwater, collected from at least ten filters with filter depths in the top 0.50 m of the groundwater over a period of 2 years with sampling each three months;
- in the soil profile, in at least five layers taken from at least 15 spots sampled at least five times including the application time.

When comparing the results of the measurements with the computed concentrations three possibilities occur:

A. the model predicts measurable concentrations in the sampled groundwater for at least one sampling time;
B. the model predicts that all concentrations are below the detection limit and also all measured concentrations are below the detection limit;
C. the model predicts all concentrations to be below the detection limit, but concentrations above the detection limit have been measured.

In case A, the test quantity is the concentration in the sampled top 0.50 m of the groundwater (the actual thickness of the sampled groundwater layer may range from 0.50- 1.0 m) averaging the results from all filters at each sampling time. The actual thickness of the sampled groundwater layer may vary between sampling times, so for each sampling time the model result will have to be based on a different thickness of the groundwater layer (this is no probem using PEARL).
The next step is to consider the time series of measured and calculated concentrations. An example is given in
Table *5*. The overall simulation error, $\overline{E_{sim}}$, is the geometrical mean of simulation errors at individual sampling times. Under the assumption of a log-normal distribution[1] of simulation errors, the geometrical mean is the best estimate for the average simulation error (Vose, 1996).

$$\overline{E_{SIM}} = \sqrt[n]{\frac{C_1}{M_1} \cdot \frac{C_2}{M_2} \cdot \frac{C_3}{M_3} \cdot \ldots \cdot \frac{C_n}{M_n}} = \sqrt[n]{\prod_{i=1}^{n} \frac{C_i}{M_i}} \qquad \textbf{Equation 3}$$

[1] The lognormal distribution is useful for modelling naturally occurring variables that are the product of a number of other naturally occurring variables. The central limit theorem shows that the product of a large number of probability distributions is lognormally distributed.

in which , i= a particular sampling time, n is the total number of sampling times, C_i is the computed concentration in the groundwater at a particular sampling time and M_i is the measured concentration in groundwater at a particular sampling time.
Equation 3 is applied using the following rules and restrictions:

1. Computed concentrations of 0.000 µg/l are expressed as <0.001 µg/l.
2. Samplings with both a computed concentration < 0.001 µg/l and measured concentrations below the limit of detection are ignored.
3. Samplings with a computed concentration of <0.001 µg/l and measured concentrations above the limit of detection result in a simulation error with a < sign.
4. If the measurement is below the detection limit, then M is set to < detection limit. If C > 0.001 µg/l, the resulting simulation error is expressed with a > sign.
5. If individual simulation errors with only > or only < signs are in the dataset, the sign should be transferred to the outcome of the overall simulation error. If both > and < signs are present in the dataset the outcome is an approximate value which could be accompanied by a ≈ sign.

The measurements should always be judged critically. For example, concentration peaks occurring in the groundwater very shortly after pesticide application, are subject to special attention. These early occurrences could be the result of e.g. sampling contamination. At the moment there is little experience with the proposed method of field experiment interpretation. The method proposed here should be evaluated when some real cases have been dealt with. The guidance given here on this subject should be considered as preliminary and should always be combined with expert judgement.

We now apply this calculation procedure to the example in
Table ***5***. Sampling 1 is ignored in view of point 2 (both the calculated concentration = 0 ànd measured concentration is below the detection limit). The mean simulation error of samplings 2 to 8 according to equation 3 is: $\overline{E_{SIM}} \approx 2.43$
This means that computed values are approximately 2.43 times the measurements. Computations for a relevant Dutch scenario will have to be divided by the simulation error of 2.43. In spreadsheets simple commands are available to calculate the geometrical mean.

Table 5 Example of calculating the simulation error for groundwater concentrations in field studies

Sampling times	Number of the sampling	Calculated groundwater concentration (µg/L)	Measured groundwater concentration (µg/L)	C_i/M_i
1-I	1	<0.001	<0.02	ignore
1-II	2	<0.001	0.03	<0.033
1-III	3	0.05	<0.02	>2.5
1-IV	4	0.22	0.12	1.8
2-I	5	0.45	0.10	4.5
2-II	6	0.53	<0.02	>26.5
2-III	7	0.47	0.06	7.8
2-IV	8	0.35	0.03	11.7

Consider case B: the model predicts that all groundwater concentrations are below the detection limit and all measured concentrations are also below the detection limit. This implies that the vulnerability of the field leaching study was less than anticipated (e.g. because of a relatively dry winter or because loss processes at the soil surface were more significant than normal). If the quality of the concentration profiles in soil is good enough, it may be possible to estimate the simulation error on calculated and measured levels at the leaching front, but this case is left to expert judgement.

Case C is not further considered here because it will often lead to a negative decision within the 2nd tier (provided that the study is classified Q1)

In addition to guidance for the summary of field and lysimeter studies, some recommendations are given for the summary of a simulation study (see **appendix 6**)

4. Conclusions

A major goal of the working group was to change over from expert judgement of lysimeter studies to a more objective evaluation. Especially for less reliable studies the conditions affecting leaching are considered in a qualitative, subjective way. An objective, quantitative and reproducible method is needed for decision making. In this report the method is elaborated for parent substances.
Lysimeter or field leaching studies are performed in order to acquire additional information with respect to leaching. The ratio between simulations and measurements is called the **simulation error**. The ratio can be used as a correction factor for the result simulated for a scenario that is relevant for the registration of a certain pesticide (**target scenario**). The simulation error can be estimated best with a study that describes all the relevant site-specific input parameters for the simulation, also DT50 and Kom determined in a parallel experiment. Only experiments describing all the relevant information for a simulation are considered to be reliable and receive the best quality index Q1. Unfortunately, many studies do not provide information on site-specific DT50 and Kom from parallel experiments with the studied soil. Because lysimeter and field studies are expensive and time-consuming, the utmost is done to interpret the results in the context of the intended registration (application). In order to be able to use these studies, the results should be extrapolated. Conservative assumptions should be made for the input data in the simulation, to compensate the uncertainty in the interpretation. This means that, in the absence of parallel experiments, the lowest DT50 and highest Kom from the dossier should be used as input for the simulation. An assumed low DT50 and high Kom result in relatively low calculated leaching, and thus a relatively low simulation error (E_{sim} =C/M). This results in a relatively high adjusted estimate in a target scenario ($C_{adjusted}=C_{target}/E_{sim}$). In this way a conservative approach in the assessment of the leaching risk is guaranteed, and it is an incentive for the applicant to improve the output of field and lysimeter studies by performing additional parallel laboratory experiments with the studied soil.

For the calculation of the simulation error, different methods are proposed for lysimeter and field studies. In lysimeter studies the accumulated leaching over the whole study period is the parameter that is compared with computed values.

$$E_{SIM} = \frac{C_{lys}}{M_{lys}}$$ **Simulation error in lysimeter studies**

In field experiments the comparison is made for the concentration in the upper groundwater at each sampling time. The geometrical mean of the ratios at all sampling times is taken as the simulation error.

$$\overline{E_{SIM}} = \prod_{i=1}^{n} \frac{C_i}{M_i}$$ **Simulation error in field studies**

Similar to building a database of DT50 and Kom values in tier 1, a database of simulation errors can be built, enabling the transparent and reproducible use of information from all the lysimeter/field experiments.
The next step in objective evaluation prescription might be the simulation of the water flow. The choices made for the simulation of water flow and water balance have much influence on the calculation of the simulation error. It is common practice to calibrate the simulation model for the

hydrology. However, this step is still not very transparent. For a better performance and judgement of simulation studies guidance for the calibration of the hydrology is needed. In this report guidance for the calibration and evaluation of the calibration is initiated. In any case a clear description of the calibration is needed. Attention should be given to parameters open for calibration, the sequence in which the parameters should be adjusted or fixed, and what the limits and stop criteria are.

The methods described in this report have been developed for parent substances. Many of the recommendations will also hold for metabolites. However conservative assumptions and vulnerability may not be equally valid for metabolites. Until now there is very little experience with the interpretation of lysimeter results of metabolites. Some case studies are required to expand the method described in the underlying report for the interpretation of leaching of metabolites.

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Appendix 1 Mailing list

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Appendix 2 Good Modelling Practice

Responsibilities of the model user

The model user must give attention to the following aspects:

Suitability of the model

- Use a version officially approved for regulatory use
- Have a good knowledge of the chemical and a good understanding of the model
- Does it include all relevant processes, and represent them in a reasonable way
- Use a scenario within the range of intended use and validity of the model. In the context of this report this means: use input (soil and climate parameters) that reflect the conditions of the lysimeter or field experiment.
- Confirm system integrity by running test input files provided and checking the results

Input data

- Choice, quality and justification of inputs to suit the chemical and scenario modelled
- Theory used in the interpretation of experimental data should be consistent with that used in the model (i.e. PEARL assumes first order exponential degradation, DT50 input must have been derived by fitting of such an equation)

Documentation and reporting

- Confirm that results are reasonable
- Document program version and date
- Detail any modifications made to the software
- Give any essential hardware/software specification
- Give all inputs used
- Where model output has been processed, give method for evaluating outputs
- Give results

Appendix 3 Recommendations for calibrating the water balance of lysimeter studies with PEARL

Introduction

The general aim is to calculate the simulation error for the pesticide or transformation product considered. The concept behind the simulation error is that PEARL does not describe the substance processes well enough because its validation status is not high enough (e.g. no accurate description of volatilisation from soil in first week after application and no description of preferential flow for structured soils) or because measuring procedures of e.g. half-lives in laboratory studies are not representative for field lysimeters. In this context it is inappropriate that errors in the description of water flow have a large influence on the simulation error. Therefore it is advisable to calibrate the simulation of water flow in the lysimeter by PEARL as good as possible. This is also consistent with procedures for model testing proposed by Armstrong et al. (1996) and Vanclooster et al. (2000). We will give guidance here on how this calibration can be best performed. Most of this guidance is based on expert judgement which should preferably be confirmed at a later stage by a sensitivity analysis of the SWAP model for water percolation from lysimeter systems.

Rainfall

Measurements of daily rainfall can only be considered accurate if the rim of the rain gauge was flush with the soil or crop surface and if the gauge was located close to the lysimeter (and not influenced by buildings other than the lysimeter station, etc.). It is well known in meteorology (already since about 1945) that the measured amount of rainfall decreases with increasing height of the rim of the gauge above the soil or crop surface; this decrease is proportional to wind speed and is more serious for snow than for rain (see Warmerdam, 1981). This experience can be illustrated with results from field experiments carried out by Alterra. E.g. Boesten (1986) found that rainfall measured at 1.2 m height in six summer months was on average 7% lower than that measured flush with the surface of bare soil. Boesten and Van der Pas (2000) found a value of 16% over a period of 1.3 year. Smelt (personal communication, 2001) found that rainfall measured at 0.4 m height was on average 15% lower than that measured flush with the surface of bare soil over a period of about 1 year. So it may be justifiable to increase the measured amount of rainfall with about 10% if it was measured between 0.4 and 1.2 m height. More serious errors can be expected if the rain gauge was placed too close to a building or any other erection that may influence the wind field around the gauge (Warmerdam, 1981) but it is difficult to give any specific guidance for such cases. If the rain gauge was placed flush with the soil or crop surface very close to the lysimeter, the rainfall measurements will be useful irrespective of the surrounding buildings.

Soil parameters

A good estimation of the soil hydraulic characteristics (soil water retention and hydraulic conductivity curves) will be crucial in many cases for a good calibration. The first step is to divide the lysimeter soil into an appropriate number of horizons. This can be based on a soil profile description and on the dry bulk density profile that can be derived from the dismantling of the lysimeter at the end of the study. If the bottom 10 cm of the lysimeter consists of fine sand to promote percolation, then this layer could be added as an additional horizon.

PEARL assumes that the soil hydraulic characteristics can be described with the Van Genuchten relationships (see Leistra et al., 2001, p. 15/16). We recommend to base first estimations of all Van Genuchten parameters on the HYPRES database (Wösten et al., 1998) which is based on measurements with soils from different European countries. Note that the Van Genuchten parameters of the Staring series as provided in the PEARL help-function are based on Dutch soils only.

A first refinement could be to estimate the saturated volume fraction of water from the dry bulk density profile of the lysimeter using a density of the solid phase in soil of 2.65 kg/L (Koorevaar et al., 1983) and assuming that the saturated volume fraction of water equals 96% of the soil porosity (N. Jarvis, personal communication 2001). For soils with organic matter contents above 5% a correction may be used, assuming 1.4 kg/L for organic matter (Koorevaar et al., 1983). A further refinement of the parameters of soil water retention curve may be obtained by calibration using the moisture profile measured at the end of the study as will be discussed later. Boesten and Gottesbüren (2000) used hydraulic characteristics measured with soil from one pit of an experimental field to simulate moisture profiles of the whole experimental field (about 0.4 ha). They found that the measurements from this single pit were not suitable for the overall field behaviour. Their experience is supported by a number of studies that show considerable spatial variability of hydraulic characteristics at a scale of 1 ha. Based on this, great care is needed when samples are taken for site-specific measurements of hydraulic characteristics of lysimeter soils. As a consequence, it is acceptable to calibrate the Van Genuchten parameters even if site-specific measurements are available.

FOCUSPEARL v1.1.1 does not include hysteresis in the soil water retention curve (Leistra et al., 2001) whereas this is optionally available in SWAP. Including hysteresis may be relevant if the simulations show wet bottom layers but percolation starts too late (absence of hysteresis in SWAP implies that the drying curve is used which is not correct for the bottom layer in wet periods). Possibly the next PEARL version will include hysteresis: this can be parameterised via only one additional Van Genuchten parameter (α for the wetting curve which can be estimated to be 2.0 times the already available value of α for the drying curve; personal communication J.C. van Dam, 1998).

As could be expected, the lower boundary condition “lysimeter” has to be used for lysimeter studies. This boundary condition implies that water can only flow out of the lysimeter and that this will only happen if the bottom compartment becomes saturated. SWAP provides a range of other lower boundary conditions which may result in a hydrologic behaviour of the lysimeter system that is not realistic.

Within SWAP, the reduction of evaporation from soil resulting from drying of the top layer is characterised by the β parameter in the soil evaporation reduction equation (see Leistra et al., 2001, p. 18 for definition of β). Boesten (1986, p. 63/64) analysed available measurements of the β parameter in the soil evaporation reduction equation (measurements of seven field soils ranging from sand to clay were available). There was no good correlation between β and soil texture. The values of β ranged from 0.54 to 0.95 $cm^{1/2}$ and we calculated an average of 0.7 $cm^{1/2}$. We recommend to use β = 0.7 $cm^{1/2}$. It is acceptable to use β as a calibration parameter but it is advised to stay within the measured range reported above. Increasing β leads to increased soil evaporation.

Parameters influencing potential evapotranspiration

It cannot be excluded that there is considerable uncertainty with respect to estimates of daily evaporation from a reference surface (shallow water for Penman equation and grass for Makkink equation; see Feddes, 1987, for description of Makking equation) even if the meteorological properties on which it was based have been measured correctly.

Within the SWAP 2.07c4 version used with FOCUSPEARL v1.1.1, the calculation of potential evapotranspiration differs between periods with and without a crop:

1. if a crop is present, the potential evapotranspiration is calculated by multiplying the reference evapotranspiration by the crop factor (see screen “Pearl - Crop Stages” of PEARL user interface)
2. if no crop is present, the potential evaporation is calculated by multiplying the reference evapotranspiration by the so-called “crop factor for bare soil” (see screen “Pearl - Soil Profiles” of PEARL user interface); its name is a little bit strange because there is no crop on bare soil (in earlier SWAP versions, it was assumed that the crop factor also applied to periods in which the soil was bare).

FOCUS (2000, p. 39) recommends a value of 1.0 for the “crop factor for bare soil” (see Penman, 1948, for an example of measurements of this factor, resulting in a range from 0.8 to 1.0 in his case).

Within SWAP the most important crop properties influencing potential transpiration are the crop factor and the leaf area index (LAI). The crop factor relates the potential evapotranspiration from a reference surface to the evapotranspiration of a full-grown crop. FOCUS (2000, p.40) has given crop factors for Penman reference evaporation (use the column called “kc_season values”) for almost all important agricultural crops. SWAP calculates first the sum of potential evaporation and transpiration and assumes further that potential evaporation from soil decreases exponentially with increasing LAI (Leistra et al., 2001, p. 17). Via this mechanism, increasing LAI leads to increasing potential transpiration. If no site-specific data are available, maximum LAI values can be derived from FOCUS (2000). Usually, the course of LAI with time is not measured in lysimeter studies. As a consequence this course can be calibrated although the course with time can only be varied within realistic bounds based on agronomic experience.

Boesten and Stroosnijder (1986) made calculations for a Dutch bare soil (six summer months) using a β value of 0.54 $cm^{1/2}$. They found that actual evaporation was about 50% of potential evaporation. For

most western European conditions, the reduction of potential transpiration will be much less than 50% (also because the lysimeters will be irrigated if there is not enough rainfall). So, increasing the contribution of crop transpiration will usually lead to decreased percolation from the lysimeter. In combination with the earlier information about the estimation of LAI this leads to the conclusion that, in general, higher LAI values will lead to less percolation.

The concept of the crop factor and the "crop factor for bare soil" has been developed for estimating evapotranspiration for agricultural areas, so areas in the order of hectares. The selected factors may not be directly applicable to small surfaces like lysimeters due to so-called "oasis" and "clothesline" effects (see Hillel, 1980, p. 209). This implies that evapotranspiration from lysimeters will be larger than expected if the lysimeter crop or soil is a moist surface in a predominant dry environment for part of the experimental period. Then additional heat will become available to the lysimeter due to local advection resulting in higher potential evapotranspiration. This is called oasis effect in case of extraction of sensible heat flowing over the top of a crop or soil surface and it is called clothesline effect in case of passage of warm air through the crop (Hillel, 1980, p.209). Hanssen (1982) studied evapotranspiration from an irrigated lysimeter (diameter 1.7 m) grown with grass and surrounded by non-irrigated grass. From his measurements it could be derived that, for periods in which the surrounding soil had a water deficit, evapotranspiration was 1.7 times as high as expected from normal crop factor values. Boesten (1994) analysed an experiment in which lysimeters with 0.3 m diameters were surrounded by bare soil and found that the crop factor was 1.5 to 2 times as large as expected. Usually, conditions of the surrounding environment over the full experimental period of the lysimeter will lead to less local advection than in the studies reported by Hanssen (1982) and Boesten (1994). A clothesline effect is unlikely for lysimeter studies submitted for pesticide registration because usually the surroundings of the lysimeter are grown with the same crop as the lysimeter. However, an oasis effect is likely to occur if lysimeter stations are located in the neighbourhood of buildings and/or hard surfaces (e.g. car parks). In conclusion, this information shows that it may be appropriate to increase the crop factor and the "crop factor for bare soil" by an oasis factor to obtain a better description of percolation. It seems defensible to vary this factor from 1 to 1.5 (depending on the characteristics of the lysimeter station).

So based on the above considerations it is acceptable to multiply both the crop factor and the "crop factor for bare soil" with a calibration factor (which should be equal for both factors). This calibration factor may account both for the uncertainty in the estimation of potential evapotranspiration and in the oasis effect. Because this calibration is no function of time, it will influence mainly the total volume of simulated water percolation and to a lesser extent the pattern of percolation (see Figs 3, 4 and 5 of Boesten, 1994, for examples). Changing the course of time of LAI will probably change both the total volume and the pattern of percolation.

Vanclooster and Boesten (2000) report that calculated cumulative actual evapotranspiration using 7 different models by in total 9 model users ranged from 398 to 549 mm for the same experimental period of the same data set. This indicates that there is in general considerable uncertainty in the estimated evapotranspiration.

Suggestions for stepwise calibration

Now we attempt to suggest a procedure for stepwise calibration of the water balance of lysimeter studies. We assume that the following measurements are available:

1. daily rainfall
2. daily estimated evapotranspiration from a reference surface
3. daily average air temperatures
4. cumulative water percolation as a function of time
5. dry bulk density profile at end of study (and % clay, silt, sand, organic matter for each horizon)
6. profile of volume fraction of liquid at end of study
7. emergence and harvest dates of crops.

The proposed procedure is as follows:

1. Check whether rainfall was measured appropriately and increase daily values if necessary (add 10% if measured above 0.4 m height).
2. Estimate all input parameters as good as possible based on the above recommendations.
3. If this results in an acceptable simulated percolation with time, then stop.
4. If not, calibrate the soil water retention curves (pF curves) as follows:
    a) calculate the saturated volume fraction of liquid for the different horizons from the dry bulk density data of the lysimeter at the end of the study
    b) calibrate the pF curves using the total amount of water in the lysimeter at the end of the study (e.g. via using PEST in combination with SWAP and allowing only the α and/or n parameters to be calibrated).
5. If the simulated percolation differs too far from the measured, calibrate the potential evapotranspiration via multiplying both the crop factor and the "crop factor for bare soil" with the same calibration factor.
6. If the percolation pattern is still not well simulated, then consider to calibrate the β parameter and/or the course of LAI with time using the measured percolation.

This procedure is tentative because we have only limited experience with calibrating the water balance of lysimeters so far.

We feel that it is not meaningful to proceed with the solute simulations if the total simulated percolation differs more than 30 mm from the total measured percolation or if the difference between these two is more than 10%. It should be always possible to obtain such small differences via adjusting the calibration factor for the crop factor and the "crop factor for bare soil". No guidance can be given at this stage whether the percolation pattern is sufficiently well calibrated.

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Appendix 4 Inverse modelling

Instead of using the simulation error as a translation factor in risk assessments, a lysimeter or field study could be used to estimate an outdoor DT50. If this DT50 is significantly different from the DT50s in the lab, this could be put forward as an argument for adjustment of the earlier risk assessment. In this case, inverse modelling is a technique of deriving the DT50 from pesticide concentrations in the leachate, considering transport and dissipation processes simultaneously. Software that optimises parameters like DT50 to fit the PEARL model to the leaching data is available. However, workshops held in 1999 and 2000 indicated that the parameters obtained by inverse modelling may be controversial. There are a lot of uncertain parameters and processes in the pesticide behaviour. By optimising the DT50 and fixing the other parameters, the uncertainty of processes and parameters is transferred to the DT50, which then becomes a lumped parameter, the result of accumulated uncertainties. Optimising several parameters simultaneously is tricky, because many of them are dependent, i.e. one parameters can compensate for the other. Until these problems are solved, parameters obtained by inverse modelling should be handled very carefully, thus invoking expert judgement.

Appendix 5 Comparison between detailed and approximate simulations

To illustrate the performance of approximate simulations four hypothetical lysimeter studies have been set up. Suppose that four undisturbed soil monoliths were taken with the characteristics of Hamburg soil. The lysimeters have been transported to different locations in order to study the effect of the application of 1 kg/ha on the 26th of May. Concentration of substance D in the leachate was simulated for four years as well as the amount of leachate. All the detailed information was available (was obtained from the PEARL database). In Table 6, an overview of the four studies and outcomes are given. As a reference, results for the Dutch standard scenario are also given.

Table 6 Overview of scenario characteristics and outcomes of four cases, calculated with PEARL 1.1.1

no.	Soil profile	Weather station (=Location of lysimeter experiment)	Crop	$C_{lysimeter}$ µg/l	amount of leachate (mm/y)
1	Hamburg soil	Chateaudun	Summer cereals	$5*10^{-5}$	108
2	Hamburg soil	Okehampton	Summer cereals	0.908	401
3	Hamburg soil	Piacenza	Summer cereals	0.013	583
4	Hamburg soil	Porto	Sunflowers	0.024	492
ref.	de Bilt	de Bilt	Maize	0.051	429

The question now is to what extent these outcomes can also be obtained by rules of thumb. Several approximations have been used to recalculate the four lysimeter studies. The starting point is the de Bilt weather station which is modified to serve as input for the lysimeter studies. So daily input of de Bilt is used in a formula to obtain a weather file that is in agreement with average annual temperature and rainfall. In these investigations irrigations were not taken into account. The following approximations have been made:

Approximation of temperature

In the summary of a lysimeter study the average annual temperature should be given (If not the summary or the underlying research report is useless). This temperature is used to correct the temperature input file in the PEARL model. The temperature input files in PEARL can be exported to a spreadsheet program and modified using the following formula.

The difference between average annual temperature in the scenario and the average annual temperature in the lysimeter is used to correct each temperature record in the input file of the PEARL scenario.

$T_{lys,i} = T_{scenario,i} + (T_{lys,\,avg} - T_{scenario,\,avg})$

This method of correction has the advantage that the number of freezing days changes and extreme records are not amplified. For example if the average annual temperature in the lysimeter experiment is 2 °C higher than the average in the PEARL scenario then each record becomes 2°C higher; -1°C → +1 °C, 20°C → 22°C.

Temperature correction of DT50

It is assumed that the reference DT50 is valid for any scenario, because the PEARL program has an internal DT50 correction based upon the temperature input file. But if the actual (or average-corrected)

daily weather input is not available one could change the reference DT50 with the Arrhenius equation so that the degradation rate is in agreement with the actual temperatures in the lysimeter. The following formula is used for the lysimeter only in combination with de Bilt temperatures input file!

$DT50_{lysimeter,\ 20°C} = DT50_{ref,\ 20°C} / e^{0.08(T,ann\ avg\ lys - T\ de\ Bilt)}$

$T_{de\ Bilt} = 9.25°C$

Approximation of precipitation

In the summary of a lysimeter study the total annual rainfall and irrigation should be given (If not the summary or the underlying research report is useless). If the study lasted for several years, then the average annual rainfall + irrigation) is used for correction of the de Bilt standard input file in the following way.

$$Precipitation_{i,\ lys} = Precipitation_{i,\ de\ Bilt} * Precipitation_{avg\ annual\ lys} / Precipitation_{avg\ annual\ de\ Bilt}$$

In this way the number of precipitation events does not change. The precipitation pattern of de Bilt is taken over except that the amount of precipitation per event changes. Extreme events are amplified. It is not possible to use a same type of formula as for the temperature correction because it could result in days with negative precipitation.

Approximation of precipitation excess

Since leaching of a pesticide is the result of downward movement, the amount of leachate from the lysimeter (=precipitation excess) may be a better parameter for correction than the amount of rainfall. Precipitation excess however is an output parameter, not an input parameter. Therefore the rainfall in the meteo input file is corrected with the following formula.

$$Precipitation_{i,\ lys} = Precipitation_{i,\ de\ Bilt} * Prec.excess_{avg\ annual\ lys} / Prec.excess_{avg\ annual\ de\ Bilt}$$

In this way the number of precipitation events does not change. The precipitation pattern of de Bilt is taken over except that the amount of precipitation per event changes.

Approximation of the ratio precipitation/precipitation excess

The ratio between precipitation and precipitation excess might give a better understanding of the extent of downward flow than precipitation excess on itself. I.e. a precipitation excess of 200 mm coming from a annual rainfall of 600 mm has another impact then the 200 mm coming from 1200 mm rainfall.

The following formulas are used to correct the rainfall in the meteo input file.

1)$R_{\text{de Bilt}}$ = Precipitation excess$_{\text{avg annual de Bilt}}$ / Precipitation$_{\text{avg annual de Bilt}}$
2)R_{lys} = Precipitation excess$_{\text{avg annual lys}}$ / Precipitation$_{\text{avg annual lys}}$
3)Precipitation$_{\text{i, lys}}$= Precipitation$_{\text{i, de Bilt}}$ * R_{lys} / $R_{\text{de Bilt}}$

Comparison of approximations

As mentioned before, the basic assumption is that a lysimeter study can best be simulated with actual daily input of temperature, rainfall, solar radiation and crop characteristics and soil profile. As output value the maximum average annual concentration has been taken. The output of the calculations with detailed input are compared with outcomes when approximations have been used. If the approximation is good, the ratio between detailed calculations and approximated calculations is 1. In Table *7* the ratios between detailed calculations and approximated calculations are given. Original concentrations and calculated precipitation excess are given in **Table 8**.

Table 7 Ratio between approximate and detailed simulations for hypothetical lysimeters

	Correction of de Bilt meteo:	Chateaudun	Okehampton	Piacenza	Porto
1	Temperature	860			
2	DT50	860	0.08	1.2	0.25
3	Precipitation	40	0.18	56	18
4	Temperature and precipitation	4	0.27	9.5	1.3
5	Crop	9820			
6	Temperature, precipitation and crop	20	0.72	33	5.0
7	Precipitation excess	-∞			
8	Temperature and precipitation excess	-∞			
9	Temperature and ratio precipitation excess/precipitation	-∞			

Because method 2 (correction of DT50 with Arrhenius-equation) was as good as changing daily temperatures for the Chateaudun climate, method 1 was not repeated for the other meteo-stations. Methods 7, 8 and 9 appeared to deviate extremely from the outcomes of the detailed calculations with the Chateaudun climate and therefore these methods were not repeated for the other meteo-stations.
It can be seen from
Table *7* that **correction of DT50 with Arrhenius** estimates maximum average concentrations from a factor 13 too low to a factor 860 too high.
Correction based on **average annual rainfall** results in estimations a factor 6 too low to a factor 56 too high.
Correction based on **average annual temperatures and average annual rainfall** results in estimations a factor 4 too low to a factor 9 too high. This methods shows the best agreement with the detailed calculations.
When besides rainfall and temperature also the actual crop was included in the model calculations estimations ranged from a factor 1.4 too low to a factor 33 too high.

Efforts to account for precipitation excess were fruitless. It resulted in extreme underestimations of maximum average annual concentrations, although (of course) the model outcome for precipitation excess matched better with the detailed calculations.
Efforts to include actual crop in approximations are not rewarded by a closer match with detailed calculations.
Based on these trials it is concluded that standardisation is very dependent upon the actual pattern of daily temperatures and rainfall. Corrections of the de Bilt meteo-input with average annual temperatures and rainfall can be made, but in critical cases a detailed calculations is indispensable.

Table 8 Overview of model input and output

Description	Meteo	crop	DT50 (days)	C_{lys} (µg/l)	Simulated prec. excess (4yr)
HC daily	Chateaudun, daily (1963-1966)	Chateaudun summer cereals	20	5.00E-05	430
HC avg temp	de Bilt temp corrected for annual avg temp in Chateaudun	de Bilt maize	20	0.043	1714
HC Arrhenius	de Bilt	de Bilt maize	16.7	0.043	1714
HC rain	de Bilt temp corrected for annual avg rain in Chateaudun	de Bilt maize	20	0.002	677
HC temp and rain	de Bilt temp corrected for annual avg temp and rain in Chateaudun	de Bilt maize	20	0.0002	677
HC crop	de Bilt	Chateaudun summer cereals	20	0.491	1717
HC temp rain crop	de Bilt temp corrected for annual avg temp and rain in Chateaudun	Chateaudun summer cereals	20	0.001	743
HC prec excess	de Bilt temp corrected for annual prec excess in Chateaudun	de Bilt maize	20	1.00^{E}-27	211
HC temp and prec excess	de Bilt temp corrected for annual avg temp and prec excess in	de Bilt maize	20	1.00^{E}-30	211
HC temp&ratio rain/excess	de Bilt temp corrected for annual avg temp and ratio rain/prec. excess	de Bilt maize	20	1.00^{E}-13	277
HO daily	Okehampton, daily (1963-1966)	Okehampton summer cereals	20	0.908	1604
HO Arrhenius	de Bilt	de Bilt maize	17.9	0.072	1714
HO rain	de Bilt temp corrected for annual avg rain in Okehampton	de Bilt maize	20	0.16	2138
HO temp and rain	de Bilt temp corrected for annual avg temp and rain in Okehampton	de Bilt maize	20	0.244	2138
HO temp rain crop	de Bilt temp corrected for annual avg temp and rain in Okehampton	Okehampton summer cereals	20	0.654	2014
PI daily	Piacenza, daily (1963-1966)	Piacenza summer cerals	20	0.013	2332
PI arrhenius	de Bilt	de Bilt maize	14.4	0.015	1714
PI rain	de Bilt temp corrected for annual avg rain in Piacenza	de Bilt maize	20	0.731	2402
PI temp and rain	de Bilt temp corrected for annual avg temp and rain in Piacenza	de Bilt maize	20	0.123	2402
PI tem rain crop	de Bilt temp corrected for annual avg temp and rain in Piacenza	Piacenza summer cerals	20	0.434	2616
PO daily	Porto, daily (1963-1966)	Porto sunflowers	20	0.024	1968
PO arrhenius	de Bilt	de Bilt maize	12.9	0.006	1714
PO rain	de Bilt temp corrected for annual avg rain in Porto	de Bilt maize	20	0.44	2138
PO temp and rain	de Bilt temp corrected for annual avg temp and rain in Porto	de Bilt maize	20	0.031	2138
PO temp rain crop	de Bilt temp corrected for annual avg temp and rain in Porto	Porto sunflowers	20	0.12	2139

Appendix 6 Guidance for summarising a simulation study

A summary of a simulation study should contain enough information to check whether the simulation was done with the right input and assumptions. For that reason the simulation study can not be separated from the lysimeter study. The evaluator must be able to check whether application rate and date, crops, soil profile and climatic conditions match to the experiment. It must be checked whether the water balance was calibrated in a satisfactory way. Also it must be verified that measured and simulated concentrations are of the same kind (accumulated, maximum or average), and not the result of artefacts, unintended contamination or preferential flow. The summary should mention what simulation package(s) have been used.
The **header** of a summary must contain the essentials of the simulation study and can be composed as follows.

Table 9 Header table of a simulation summary

compound	type	package	Simulated parameter	SE[1]	Q
parent	simulation	PEARL 1.1.1	Accumulated leaching	0.1	1
metabolite A	simulation	PEARL 1.1.1	Accumulated leaching	0.01	2

[1]SE=simulation error

The **description** of the summary must specify how the choice of DT50 and Kom for the simulation was made.
If these major input parameters are not site-specific but taken from a dossier, mention the range of values from which the values have been picked and the reasons for a particular choice. In the absence of site-specific input parameters conservative choices must be made. This means a low DT50 and a high Kom for C_{lys}, because that results in conservative (=relatively high) simulation errors. A table like Table 10 may be convenient.

Table 10 Summary table of simulation input/output

	DT50	Kom	Dosage	Application date	C leach
M_{lys}	n.r.	n.r.			
C_{lys}					
C_{DUS}					

Under **"remarks"** special attention should be given to the possible shortcomings of the study. In §3.3 and §3.4 the recommended procedures are described.