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Recommendations for Simulation Calculations of Predicted Environmental Concentrations in Ground Water (PECgw) in the National Authorisation Procedure

Empfehlungen für Simulationsrechnungen im nationalen Zulassungsverfahren zur Prognose der Wirkstoffkonzentration im Grundwasser (PECgw)

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Abstract

In the national authorisation procedure the leaching behaviour of a plant protection product is determined in a stepwise procedure. The first step is an estimation of the leaching potential of the respective active substance by means of a simulation calculation. These calculations, which are performed using the PELMO 3.0 model, are triggering multi-year field lysimeter studies. This paper will provide specific recommendations that permit a definite determination of the input data required for the simulation model. The degradation behaviour of the active substance and its metabolites in soil is parameterised dependent on the number of DT_{50} values and their coefficient of variation. Most data sets will allow for the use of the geometric mean or the median value. DT_{50} values from field tests may be used in the model after normalisation for soil temperature and soil moisture. The sorption behaviour is simulated with the arithmetic mean of individual K_{foc} values and Freundlich exponents if adsorption is correlated with the organic carbon content in soil. Horizon specific adsorption coefficients, which are to be detemined by regression analysis of available sorption data or by specific experiments with subsoil samples, have to be used in all other cases.

Key words: Simulation model, PELMO, leaching, groundwater, plant protection product, parameterisation, normalisation, authorisation procedure

Zusammenfassung

Im nationalen Zulassungsverfahren wird das Versickerungsverhalten eines Pflanzenschutzmittelwirkstoffs nach einem gestuften Verfahren ermittelt. Dabei wird das Versickerungspotential des jeweiligen Wirkstoffs im ersten Schritt mit Hilfe von Simulationsrechnungen abgeschätzt. Die Berechnungen, die mit dem Modell PELMO 3.0 durchgeführt werden, können mehrjährige Freiland-Lysimeterstudien auslösen. Mit der vorliegenden Arbeit werden konkret umsetzbare Empfehlungen gegeben, die eine möglichst eindeutige Ermittlung der für die Modellsimulation notwendigen Eingabedaten ermöglichen. Das Abbauverhalten des Wirkstoffs und seiner Metabolite im Boden wird in Abhängigkeit von der Anzahl der Einzelwerte und ihres Variationskoeffizienten parametrisiert. In der Mehrzahl der Fälle erlauben die Datensätze die Verwendung des geometrischen Mittelwertes oder des Medianwertes. DT_{50}-Werte aus Feldversuchen können nach Normierung der Bodentemperatur und -feuchte im Modell verwendet werden. Die Adsorption wird mit dem arithmetischen Mittelwert der einzelnen K_{foc}-Werte und Freundlich-Exponenten simuliert, sofern eine Korrelation der Adsorption mit dem organischen Kohlenstoffgehalt des Bodens vorliegt. In allen anderen Fällen müssen horizontspezifische Adsorptionskonstanten benutzt werden, die entweder durch Regressionsanalyse mit vorhandenen Sorptionsdaten oder experimentell an Unterbodenproben ermittelt werden.

Stichwörter: Simulationsmodell, PELMO, Versickerung, Grundwasser, Pflanzenschutzmittel, Parameterisierung, Normierung, Zulassungsverfahren

I Introduction

The following recommendations for performing simulation calculations of the leaching behaviour of active substances in plant protection products for the national authorisation procedure were developed for the PELMO 3.0 model (JENE, 1998; KLEIN, 1995). This publication is meant to supplement and clarify earlier recommendations (FOCUS, 2000; RESSELER et al., 1997). Reference is made to definitions provided therein. Clear procedures for parameter selection are proposed below. However, a discussion of statistical methods is not given. In specific or borderline cases, consultation with the competent authorities is recommended since it is impossible to cover every possible case within the scope of this publication.

In the national authorisation procedure, the **PELMO 3.0** model is used in the manner described here for calculating the PECgw since a sufficiently conservative estimate of leaching behaviour has been demonstrated for this procedure by comparisons with results from numerous lysimeter experiments (FENT et al., 1998; JENE et al., 1999; KLEIN et al., 2000; IVA, 2002). The lysimeter study as described by SCHINKEL (1991) represents a higher testing level in the national authorisation procedure than the calculation.

On the European level, FOCUS groups (FOCUS = FOrum for the Coordination of pesticide fate models and their USe), e.g.

FOCUS Kinetics, are working on recommendations for deriving kinetic parameters from laboratory and field studies which may in future become relevant also to the national authorisation procedure.

II General Recommendations on Parameter Selection

In the national (German) and European (EU) procedures, the values of 2.2 for Q_{10} and 0.7 for B (Walker exponent) are uniformly used. These are based on FOCUS (1996) and have been adopted by FOCUS (2000). The calculation of metabolite formation and degradation is based on ERZGRÄBER et al. (2002).

III Special Recommendations on Parameter Selection in PELMO 3.0 Calculations Using Hamburg Reference Climate and Borstel Reference Soil

1 Aerobic Soil Degradation

1.1 General Requirements for the Suitability and Selection of the DT_{50}

Most data sets will allow for the use of the geometric mean or the median value of the DT_{50} for model input (see chap. 1.2). DT_{50} values with a high variance, however, must be given careful consideration.

High variance is defined with reference to FOCUS, 2000 (chap. 6.4.6) as a coefficient of variation of $\geq 100\%$. If DT_{50} values exhibit such a high variance, the 90th percentile of DT_{50} values is used in the simulation model instead of the average DT_{50} value, as will be described in more detail below. In case of concurrent simulation of the leaching behaviour of active substance and metabolites, an additional simulation run using the 10th percentile of the parent substance's DT_{50} has to be performed. Other metabolite formation and degradation values remain unchanged.

Studies with experimental artefacts are invalid and should be excluded from further consideration in the simulation. Justification for exclusion has to be provided. DT_{50} values from experimentally valid studies which are not reflecting the intended use under assessment (see examples below) also have to be excluded from the calculation of the variation coefficients, mean/median values and percentiles. Justification for exclusion has to be provided.

A conservative approach should be followed when excluding studies and reliable justification should be given. Exclusion could for example be justified if the following test conditions occurred (given that those conditions have a clear influence on the DT_{50} and are not relevant for the intended use):

● Tests conducted on soils with very high organic carbon content (e.g. marsh, forest or volcanic ash soils);
● Tests conducted on grassland soils with very high microbial activity which is not comparable to that of arable soils;
● Significant overdosing of the test substance;
● Strong decline of microbial activity in laboratory tests during the test period.

In case of doubt whether a value should or should not be excluded from further consideration, consultation with the competent authorities is recommended.

DT_{50} values from laboratory studies are used as model input for calculations at tier 1 of the exposure assessment. If under these conditions no maximum annual concentrations > 0.1 µg/L are predicted, no further calculations are required.

The use of DT_{50} values from field studies is possible in justified individual cases in the context of tier 2 simulations. Tier 2 simulations must be clearly marked as such. Field tests must ad-

here to BBA Guidance (Guideline IV 4-1 level 2 (1986)) or to the SETAC Guidance (1995). Substance-specific features must be taken into account when entering data (e.g. by switching off volatilisation when using field data (FOCUS 2000, chap. 5.4.2)). Furthermore, certain requirements must be met when using the DT_{50} values for input into the model. The criteria were compiled based on a checklist published by the Dutch competent authority (CTB, 1999; quoted in FOCUS, 2000, chap. 5.5. p. 87).

Criteria that field degradation studies must meet to enable the use of the respective DT_{50} as an input value in the simulation calculation include:

● The degradation of the active substance during the test period should correspond reasonably well with first-order kinetics. If this is not the case, it should be checked whether the dissipation of the substance in the field degradation study is due to significant volatilisation or photolysis and therefore requires a modified assessment. This should include consideration of the time period between the application and the first significant precipitation event as well as consideration of recovery and of the course of degradation kinetics. Rapid initial degradation followed by significant deceleration may indicate dissipation by volatilisation and/or photolysis.
● It must be confirmed that the dissipation of the substance during the field degradation study is not the result of plant uptake to any significant extent.
● It must also be confirmed that the dissipation of the substance during the field degradation study is not due to significant leaching into soil horizons below the sampled soil layer (measured concentrations in the deepest sampled soil layer and the influence of heavy precipitation events should be taken into account).
● Soil properties and climatic conditions must be described to a sufficient extent (BBA Guideline, 1986; RESSELER et al., 1997; SETAC, 1995). Meteorological data must be available for the whole study period. The amounts tested should reflect the application rate of the intended use under consideration.
● The test should not be conducted with a granular or "slow release" formulation. Recovery must be sufficient, sampling and analytical detection methods must be appropriate.
● The substance must not be incorporated into the soil unless this is in accordance with GAP. Neither the test substance nor an analogous active substance should have been used in previous years at the study location.
● The evaluation period should continue at least until the DT_{75} has been reached.

1.2 DT_{50} from Laboratory Studies

When the number of studies and DT_{50} values is available which is required as a minimum according to Guideline 91/414/EEC (95/36/EC) (active substance: 4 values, metabolite: 3 values; the same procedure applies to 5 values for the active substance and 4 values for the metabolite), the geometric mean of the k-rates of the DT_{50} values is employed based on the recommendations of FOCUS, 2000. If less values are available (active substance: < 4 values, metabolite: < 3 values), the highest DT_{50} value is used. If more values are available (active substance: ≥ 6 values, metabolite: ≥ 5 values), the median of the k-rates of the DT_{50} values is used (based on FOCUS, 2000 and RESSELER et al., 1997).

The temperature is normalised to a reference temperature of 20 °C if the laboratory test has an incubation temperature other than 20 °C.

As standard the soil moisture is not normalised to a specific reference moisture. Instead the experimental moisture value (BBA Guideline IV, 4-1 regarding active substance degradation testing, 1986) is employed in PELMO 3.0 as reference moisture

relative of the maximum water holding capacity (e.g. 40 % or 50 % MWHC; displayed as 40 % or 50 % FC in the PELMO 3.0 sp 2 input face; JENE et al., 1998) or as absolute moisture. A moisture content of 40 % MWHC was also used in the PELMO validation experiments (JENE et al., 1998).

No moisture normalisation is performed if the water content of the soil during incubation lies within the relatively narrow range of 40 to ca. 50 % of the maximum water holding capacity. This moisture range was also proposed in the SETAC Guidance (1995). If studies with clearly deviating soil moisture conditions (e.g. according to the US EPA Guideline) are intended to be used, this would require a specific justification.

1.3 DT_{50} from Field Studies

When the number of studies and DT_{50} values is available, which is required as a minimum according to Guideline 91/414/EEC (95/36/EC) (active substance: 4 values, metabolite: 3 values; the same procedure applies to 5 values for the active substance and 4 values for the metabolite), the geometric mean of the k-rates of the DT_{50} values is employed based on the recommendations of FOCUS, 2000. If less values are available (active substance: < 4 values, metabolite: < 3 values) the highest DT_{50} value is used. If more values are available (active substance: ≥ 6 values, metabolite: ≥ 5 values) the median of the k-rates of the DT_{50} values is used (based on FOCUS, 2000 and RESSELER et al., 1997).

In field degradation studies, metabolite degradation often can not be clearly determined in statistical terms due to low concentrations and low sampling frequencies. The ratio of degradation rates of active substance and metabolite is therefore in these cases transferred from the laboratory to the field study. However, if field data are supposed to be used for the metabolite, this requires specific justification and discussion with the competent authorities is recommended.

There are several options for entering the field degradation data into the model, which are explained in the following.

1.3.1 Reference temperature and temperature correction

a) If the field DT_{50} value was obtained from a study performed according to the GAP and under temperature, moisture and soil conditions equivalent to those in the Hamburg reference scenario, this DT_{50} value may be entered directly into the model. Temperature and moisture correction functions need to be deactivated.

b) If the climate at the field location is not directly equivalent to the Hamburg reference scenario, but is representative of other prevailing conditions in Germany, the following procedures may be applied:

● Field DT_{50} values may be normalised to a reference temperature (e.g. 20 °C) by normalising each single measurement based on measured daytime soil temperature or on corresponding air temperature, respectively. From the latter, soil temperature can be calculated. Reference soil moisture values might be taken from published literature as long as they can be considered conservative. Measured or simulated soil moisture values may also be used to calculate moisture normalised DT_{50} values analogous to the temperature normalisation. In all these cases, the values are used directly in the model. The temperature correction function must be activated if normalised DT_{50} values are used.

● If the substance degrades rapidly, i.e. if the DT_{90} value is reached within four weeks and if no significant change of temperature occurred during this period, a simplified normalisation procedure may be used. Instead of daily corrected values, a representative average temperature may be derived for the field test and entered into the model. In this

case the temperature correction function of the model remains activated.

If degradation data from more than one field study have been normalised, the geometric mean or median of the normalised field DT_{50} values may be entered into the model (same procedure applies as for laboratory data). If less studies and DT_{50} values are available than required as a minimum according to Guideline 91/414/EEC (95/36/EC) (active substance: < 4 values, metabolite: < 3 values) the highest DT_{50} value is used. The respective correction functions of the model remain active.

Detailed information concerning the normalisation of field DT_{50} valuses to reference conditions is given in Chapter VI (Appendix).

1.3.2 Reference moisture and moisture correction

If the field DT_{50} value was obtained from a study performed according to the GAP and under temperature, moisture and soil conditions equivalent to those in the Hamburg reference scenario, this DT_{50} value may be entered directly into the model. Temperature and moisture correction functions need to be deactivated.

Reference soil moisture values might be taken from published literature as long as they can be considered conservative. Measured or simulated soil moisture values may also be used to calculate moisture normalised DT_{50} values analogous to the temperature normalisation. In all these cases, the values are used directly in the model. The moisture correction function must be activated if normalised DT_{50} values are used.

2 Adsorption

A precondition for the procedure described in the following is the availability of adsorption data for the active substance from at least 4 soils (metabolite: at least 3 soils) that have been determined according to OECD Test Guideline 106. Otherwise, the adsorption data of the soil that will result in the most conservative estimate of active substance concentration in the groundwater must be used.

The arithmetic mean of the K_{foc} values and of the Freundlich exponents (1/n) of all soils are used as entry parameters for the simulation model (activation of the "K_f value – calculated with K_{foc}" function in PELMO), if a clear correlation between the adsorption coefficient K_f and the organic carbon content of the soils exists (guideline value: correlation coefficient of r ≥ 0.7). Soils with an organic carbon content of less than 0.3 % are not used in the modelling.

If the correlation coefficient of the K_f value and the organic carbon content lies below the guideline value of 0.7, the correlation of K_f with other soil properties such as clay content, cation exchange capacity (CEC) and pH value has to be checked. If the correlation of the K_f value with any other soil parameter is higher than the correlation coefficient of the K_f value with organic carbon content, use of the K_{foc} value is not appropriate. Instead, horizon-specific K_f values are used (activation of the "K_f value – direct input" function in PELMO).

If a correlation with the clay content or cation exchange capacity of the soil exists, the K_f values are determined for each horizon by means of the respective correlation equation and the properties of the reference scenario soil Borstel and then entered into the model. No information is given, however, about the cation exchange capacity in the Borstel soil scenario (KLEIN, 1995). It is recommended to use values which have been measured in lysimeter studies with the Borstel soil, i.e. 7.5, 3.9, 2.4, 0.9, and 0.8 meq/100 g dry soil for the soil horizons of 0–30, 30–60, 60–75, 75–90 and 90–110 cm, respectively.

In case of a clear correlation of the sorption of the respective substance with the pH value, the lysimeter soil does not necessarily represent a (conservative) weak sorption soil for this substance. In such cases, the K_f value of that soil is selected for input into the model that represents a realistic worse case concerning the leaching behaviour of the substance.

For example the sorption behaviour of a dissociating substance (weak acid) should be described by a worst case K_{foc} value that was determined in a soil with pH > 7. At the same time, the default value of pKa = 20 in PELMO remains unchanged for dissociating and non dissociating substances.

If a good individual correlation cannot be found, the presence of a multiple correlation of the K_f value with several soil properties should be considered. Depending on the correlation, appropriate "realistic worst case" K_f values should be determined specific to the horizon by means of the specific correlation equation and the properties of the reference scenario soil Borstel ("K_f value – direct input" in PELMO).

If the K_f values are not sufficiently well represented by a correlation equation with several soil properties, experimentally determined horizon-specific K_f values may be entered.

Independent of the stepwise scheme described here, it is always possible to enter experimentally determined horizon-specific K_f values directly into the model (activation of the "K_f value – direct input" function in PELMO), given that these values have been determined in a soil profile that leads to a weak adsorption of the test substance and thus represents a realistic unfavourable case.

3 Simultaneous Effect of the pH Value on Degradation and Sorption

Both sorption and degradation behaviour of an active substance or a metabolite in soil may be pH dependent. Additive effects may arise causing both a reduction of sorption and degradation rates in soil. This must be accounted for when selecting appropriate input parameters.

Parameters should be selected carefully in a way they represent an overall realistic worst case. Unrealistic combinations must be avoided, e.g., low sorption coefficients determined in an alkaline soil must not be combined with large DT_{50} values determined in an acidic soil.

4 Other Input Parameters

Application amounts:
The maximum annual application amount and the date(s) of application must be simulated according to GAP. In case of different application amounts and different options for crop rotation it is sufficient to simulate the worst case GAP/crop rotation scenario with respect to the amount of active substance reaching soil (after consideration of crop interception). Annual application is simulated for permanent crops, while for rotational crops applications are simulated in accordance with the position of the treated crop in the crop rotation sequence.

Crop interception:
The real amount of active substance reaching soil is derived from the maximum application amount reduced by crop interception if plants are present at the time of application. A detailed overview of applicable crop interception factors has been prepared by the FOCUS groundwater working group (FOCUS, 2000). Updates of these factors are published in the

Generic Guidance Paper at the ISPRA FOCUS website (www.viso.ei.jrc.it/focus/).

Soil:
The Borstel reference soil profile is used down to a depth of 1.1 m with the biodegradation factors given in the PELMO 2.01 manual (KLEIN, 1995).

Simulation period:
A simulation period of ten years is normally used (RESSELER et al., 1997). The simulation period must be prolonged if the concentration in leachate increases over the default ten-year period.

Climate:
For the simulation period the climate files of Hamburg 1961 ("wet", 872 mm, 9.1 °C) and Hamburg 1978 ("normal", 778 mm, 8.3 °C) (cf. Pelmo 2.01 manual, KLEIN, 1995) are used alternatingly (RESSELER et al., 1997).

Plants:
The plant scenarios and Haude factors (in crop rotation, if applicable) are used according to the PELMO 2.01 manual (KLEIN, 1995).

Evapotranspiration:
Evapotranspiration is considered according to the Haude equation (PELMO 2.01 manual, KLEIN, 1995).

Erosion, runoff, and volatilisation:
These processes are not accounted for in the simulations and the corresponding submodules are deactivated. According to the model, the amount of substance reaching the soil is only subjected to degradation and leaching.

Pesticide uptake:
For active ingredients which are not taken up via the roots, normally non systemic active substances, the "pesticide uptake factor" in the scenario file is set to zero (TSCF = 0). Otherwise a factor of 0.5 is recommended according to FOCUS (2000).

IV Assessment of Simulation Results

Main simulation results are the average annual concentrations of the active substance and/or metabolite(s) in the leachate (in µg/L) at a depth of 1.1 m. The maximum annual average concentration is selected as the critical endpoint of the assessment. This value represents the individual PEC_{gw} for each compound. Averages must not be calculated over several years.

In the case that the simulation-based PEC_{gw} of the active substance is > 0.1 µg/L, a field lysimeter study is required as higher-tier study. This study is considered superior to the simulation, and concentrations determined in the study take precedence over calculated concentrations. The concentrations which are relevant for decision-making are derived for lysimeter studies in an analogous manner to the approach described for simulation calculations: the highest measured average annual concentration in a single lysimeter is the regulatory endpoint (BBA IV, 4–3, "Lysimeter Guideline" (BBA, 1990); Modification of the Lysimeter Guideline (SCHINKEL, 1991), Announcement on the assessment of lysimeter results in the Federal Gazette (KOHSIEK, 1997), JENE et al., 1998 (SLFA Project Report)).

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VI Appendix

Normalisation of field DT$_{50}$ values to reference conditions

Introductory remark

Field DT$_{50}$ values can be used as input parameters for PELMO 3.0 calculations (with justification, see chap. III 1.1, 1.3). It may be necessary, as decribed under III 1.3.1, to normalise field DT$_{50}$ values to reference temperatures and moistures (usually 20 °C and 100 % FC). It must be stressed that normalised field data can not be used for assessing the degradation behaviour (i.e. not as persistence triggers or for triggering of ecotoxicological tests). The normalised formation rates of metabolites should be exclusively used as input parameters in models, which are able to simulate daily variations of temperature and soil moisture. The normalised rate is not appropriate for assessing the dissipation during the field test itself, because the site-specific climate pattern is no longer reflected after normalisation. The normalised field half-life represents a rate at 20 °C and 100 % FC (at 10 kPa) whereas uncorrected rates reflect local temperature and soil moisture conditions.

In the following chapter, two conceptually similar approaches for normalisation are presented. The first method corrects field half-lives by increasing or decreasing day-lengths; the second approach corrects degradation rates directly.

Method 1: Day-length correction

The normalisation is done by reducing or increasing day lengths depending on soil temperature and moisture by means of correction factors identical to those used in most regulatory leaching models.

$$D_{Norm} = D \cdot f_{temp} \qquad \text{(eq. 1)}$$
$$f_{temp} = Q_{10}^{(T-T_0)/10} \qquad \text{(eq. 2)}$$

Where:
D_{Norm}	= Normalised day length
D	= 1 d
f_{temp}	= Correction factor for soil temperature
Q_{10}	= 2.2 (FOCUS, 2000)
T	= Actual soil temperature
T_0	= Reference soil temperature (e.g. 20 °C)

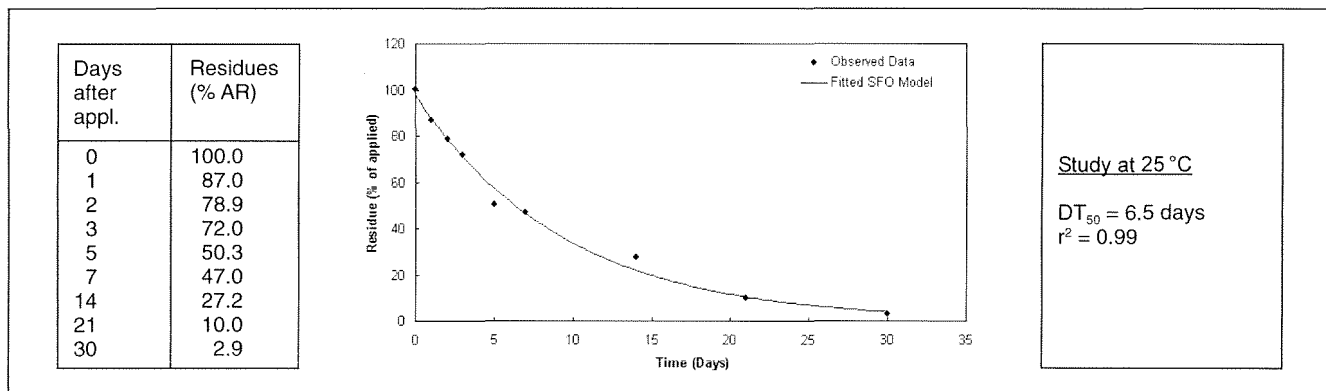| Days after appl.	Residues (% AR)
0	100.0
1	87.0
2	78.9
3	72.0
5	50.3
7	47.0
14	27.2
21	10.0
30	2.9

Study at 25 °C

$DT_{50} = 6.5$ days
$r^2 = 0.99$

Fig. 1. Laboratory degradation at 25 °C.

$$D_{Norm} = D \cdot f_{moisture} \qquad \text{(eq. 3)}$$

$$f_{Moisture} = \left(\frac{theta_{actual}}{theta_{reference}} \right)^{0.7} \qquad \text{(eq. 4)}$$

Where:
D_{Norm} = Normalised day length
D = 1 d
$f_{moisture}$ = Correction factor for soil moisture
$theta_{actual}$ = Actual soil moisture (v/v)
$theta_{reference}$ = Reference soil moisture (= v/v at field capacity)

Cumulative corrected day lengths are calculated between each sampling interval to result in 'normalised' days after applications. The practical impact of the normalisation procedure is that days with an average soil temperature > 20 °C are longer whereas days with temperatures < 20 °C are shorter than reported days after application. Days with soil moisture contents less than the reference soil moisture will become shorter. The normalised day scale and residue data for parent compounds and metabolites may then be re-analysed to obtain kinetic parameters used in leaching modeling on the basis of field data. Note that the Q_{10} response function is only applied for temperatures above 0 °C. As a consequence it is assumed that no degradation occurs below 0 °C.

In cases where soil temperature data is not available, average daily soil temperatures may be estimated on the basis of daily air temperature measurements, using the algorithm implemented in PELMO 3.0, or similar leaching models. The extrapolation of air temperature is done for a specified soil depth. It is therefore recommended to identify the soil layers where the bulk mass of the pesticide under investigation was present in the study period and select the respective soil depth for the extrapolation.

Equation 5 shows the algorithm, which is implemented in PELMO 3.0 to calculate soil temperatures. In accordance to the approach taken in PELMO 3.0 it is further recommended to use the air temperature on the first day of the simulation as a starting value.

$$T = T_{prev} + \left(T_{air} - T_{prev} \right) \cdot 0.346 \cdot \exp(-0.027028 \cdot d) \qquad \text{(eq. 5)}$$

Where:
T_{prev} = Soil temperature of previous day
T_{air} = Daily average air temperature
d = Depth of soil compartment, depth in which the bulk of pesticide mass was detected

Like soil temperature, soil moisture data is not readily available for many field soil dissipation experiments. A constant soil moisture of 100 % FC during the study period may be used in a very conservative approach. For a more realistic assessment, average daily soil moisture contents may be estimated with leaching models like PELMO 3.0. As for soil temperature, it is recommended to identify the layer where the bulk mass of the pesticide under investigation was present during the study period and to predict daily soil moisture contents for that layer for the normalisation.

Validity check of the day-length correction method

The first example illustrates the validity of the concept of normalised day lengths. A laboratory study conducted at 25 °C resulted in the decline curve of the parent compound over a period of 30 days as shown in Figure 1. The degradation

Days after appl.	Residues (% AR)
0	100.0
1.5	87.0
3.0	78.9
4.4	72.0
7.4	50.3
10.4	47.0
20.7	27.2
31.1	10.0
44.4	2.9

Study normalised to 20 °C

$DT_{50} = 9.6$ days
$r^2 = 0.99$
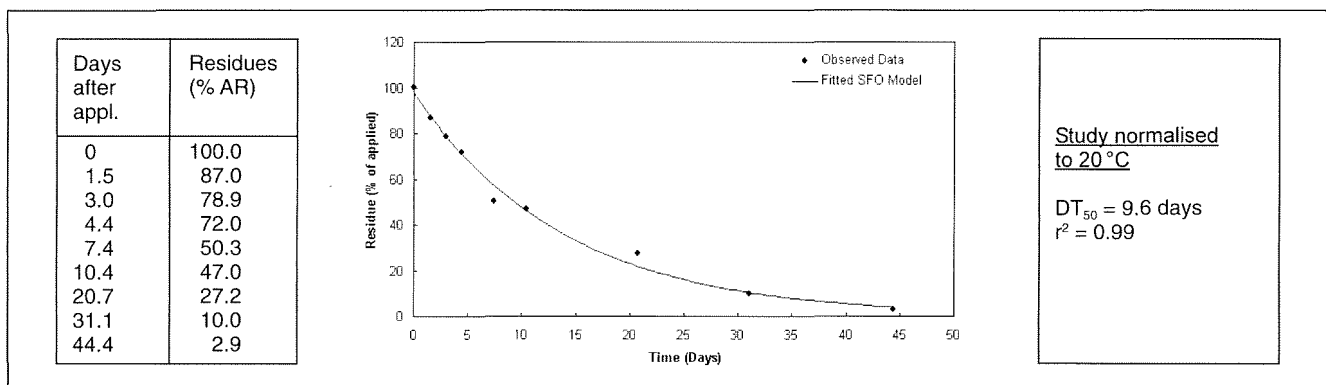
Fig. 2. Normalised laboratory degradation at 20 °C

Fig. 3. Example data sets.

Method 2: Direct normalisation of degradation rates

A direct normalisation of degradation rates can be performed by incorporating the Arrhenius approach (see eq. 2) in a Model-Maker® model. During the kinetic fitting procedure, Model Maker® accounts for daily temperature variations and thus provides a first-order field dissipation half-life at 20 °C (for the compartment model used for the fitting procedure see Figure 6).

Daily degradation rates are corrected by means of a correction factor f temp., (equation 6). Multiplying the fitted degradation rate at reference temperature (k_{Tref}) with the respective correction factor (equation 6) eventually yields the degradation rate at actual temperatures (k_{Tact}). Again it is assumed that degradation occurs only at temperatures > 0 °C.
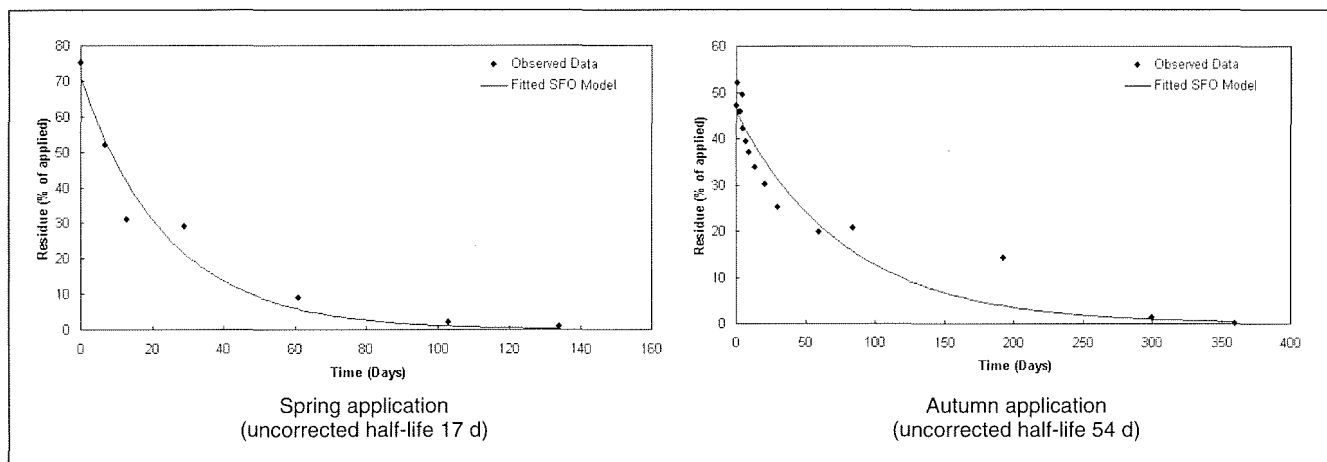
clearly follows single first-order kinetics; the corresponding DT_{50} value is 6.5 days. A conventional normalisation to 20 °C results in a half-life of 9.6 days [6.5*(2.2^((25-20/10))]. When applying the conceptual approach which was described above, the day length for each day of the study is (2.2^((25-20/10)) = 1.48 days. As a consequence the approach gives rise to normalised cumulative days after application as shown in Figure 2. Again, the degradation follows single first-order kinetics, the corresponding DT_{50} value is 9.6 days, identical to the value of the conventional approach. It can therefore be concluded that the normalisation of day-lengths leads to the same result as the standardised normalisation of laboratory half-lives.

Days after appl. Reported	at 20 °C	Residues (% AR)
0	0.0	75
7	4.5	52
13	9.4	31
29	21.0	29
61	42.9	9
103	84.5	2
134	111.9	1

Study normalised to 20 °C

DT_{50} = 12.1 days
r^2 = 0.96

Day-length normalisation

Days after appl. Reported	at 20 °C	Residues (% AR)
0	–	75
7	–	52
13	–	31
29	–	29
61	–	9
102	–	2
134	–	1

Study normalised to 20 °C

DT_{50} = 12.5 days
r^2 = 0.95

Rate normalisation

Fig. 4. Normalised field dissipation half-life at 20 °C following spring application.

Days after appl. Reported	at 20 °C	Residues (% AR)
0	0.0	0.0
1	0.3	0.3
2	0.7	0.7
3	1.0	1.0
4	1.3	1.3
5	1.9	1.9
7	2.9	2.9
9	3.7	3.7
14	5.5	5.5
21	8.3	8.3
30	10.7	10.3
60	17.9	15.2
84	22.0	16.4
193	40.7	24.4
300	78.0	59.3
360	108.7	90.1

Observed Data
Fitted SFO Model

Study normalised to 20 °C

$DT_{50} = 11.9$ days
$r^2 = 0.98$

Day-length normalisation

Days after appl. Reported	at 20 °C	Residues (% AR)
0	–	0.0
1	–	0.3
2	–	0.7
3	–	1.0
4	–	1.3
5	–	1.9
7	–	2.9
9	–	3.7
14	–	5.5
21	–	8.3
30	–	10.3
60	–	15.2
84	–	16.4
193	–	24.4
300	–	59.3
360	–	90.1

Parent

Study normalised to 20 °C

$DT_{50} = 11.3$ days
$r^2 = 0.98$

Rate normalisation
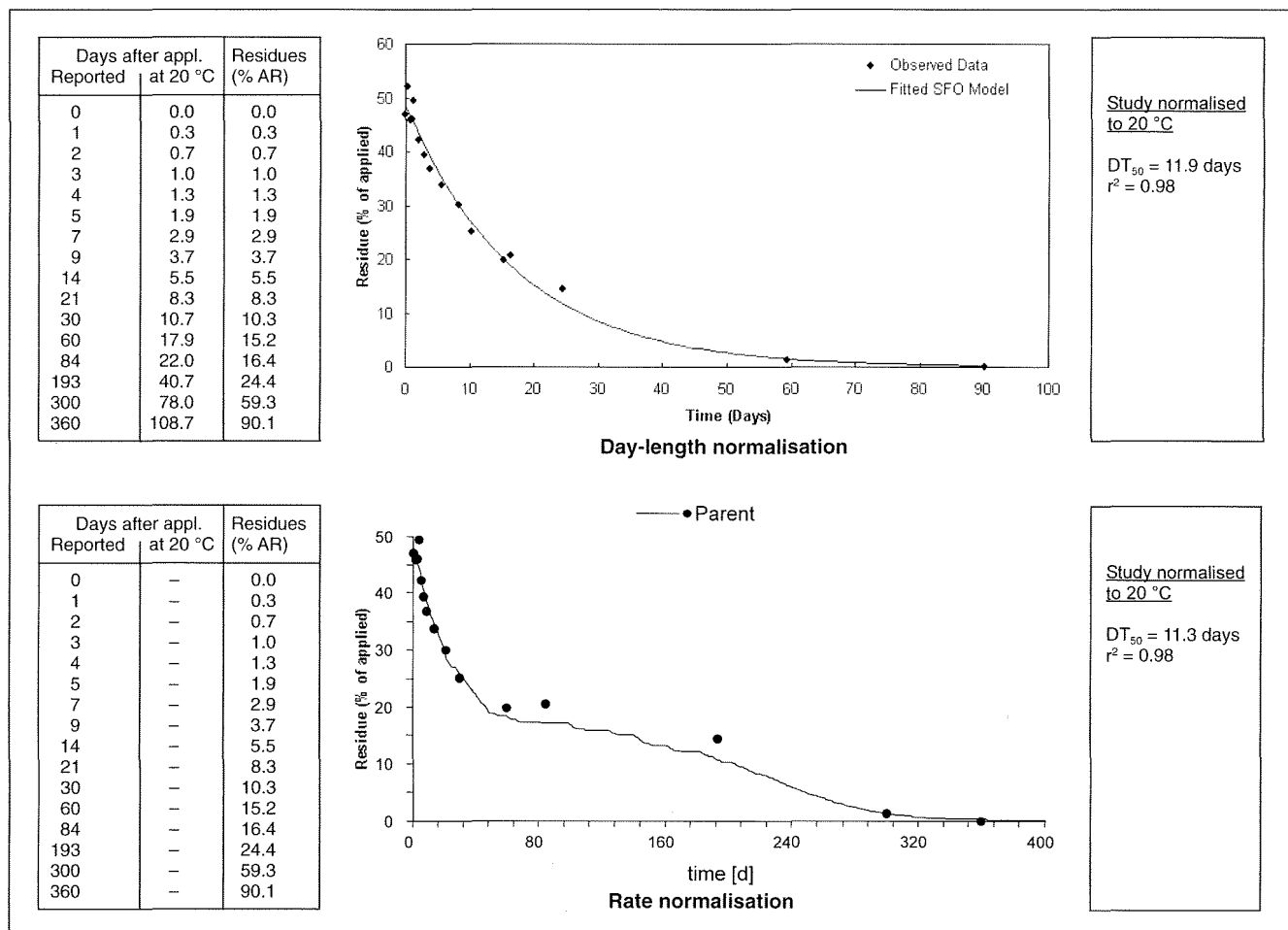
Fig. 5. Normalised field dissipation half-life at 20 °C following autumn application.

$$f_{temp} = 0 \qquad for \ T_{act} \leq 0 \ °C$$

$$f_{temp} = Q_{10}^{\frac{Tact-Tref}{10}} \qquad for \ T_{act} > 0 \ °C \qquad (eq. \ 6)$$

$$k_{Tact} = k_{Tref} \cdot f_{temp}$$

Where f_{temp} = Temperature correction factor [-]

k_{Tact} = Degradation rate constant at actual [1/d]
temperature T act

k_{Tref} = Degradation rate constant at a refe- [1/d]
rence temperature T_{ref}

T_{act} = Actual temperature [°C]

T_{ref} = Reference temperature (20 °C) [°C]

Q_{10} = Factor of increase of degradation rate [-]
with an increase in
temperature of 10 °C (Q_{10} = 2.2, FOCUS
recommendation)

In accordance to method 1, all temperatures refer to soil temperatures. In cases where the respective soil temperatures are not available, equation 5 should be applied to derive an estimate on soil temperatures.

Unlike standard first-order fits, the inclusion of daily temperature fluctuations does not result in smooth curves. The slope of the dissipation curves usually flattens during cooler periods

whereas higher temperatures lead to a more pronounced slope. In this way the curve realistically reflects the effect of the temperature fluctuations during the study with higher degradation rates in warmer periods and lower degradation rates in cooler periods.

Comparison of Methods 1 and 2

In principle methods 1 and 2 should lead to similar results since both methods are based on the same conceptual approach, i.e.,

Parent

F.12 ◄··· kact ·······◄···· T1

C2_EliminationCompartment

optimization:
-temperature correction is implemented (register report)
-initial concentration d1 is estimated (start value 100)
-start value transformation parameter is 0.01
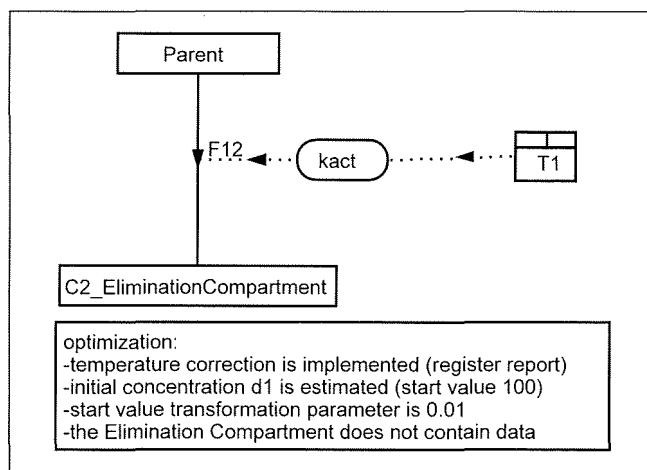-the Elimination Compartment does not contain data

Fig. 6. Symbolic representation of the compartment model used.

the Arrhenius relationship as used in PELMO 3.0. To illustrate the inherent similarity of both methods, the two field dissipation studies are normalised to 20 °C using methods 1 and 2, respectively. The first study represents a spring application whilst the second study was initiated in autumn (Figure 3). In both cases it was assumed that soil moisture was constant at 100 % FC; however, variations of soil moisture are considered in the same way as temperature variations. The uncorrected field dissipation half-life for the spring test is 17 days; for the autumn test, the uncorrected half-life is 54 days. Both the daily correction of degradation rates as well as the correction of day-lengths yield similar half-lives: 12.1 days compared to 12.5 days for the spring application and 11.9 days compared to 11.3 days for the autumn application (Figures 4 and 5). The differences between the methods are very small and still within the numerical accuracy of kinetic fitting programs as indicated by the respective confidence limits.

It is therefore concluded that both methods result in equally valid results.

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SABINE REDLHAMMER (Braunschweig)