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Soil persistence models and EU registration

The final report of the work of the Soil Modelling Work group of FOCUS (FOrum for the Co-ordination of pesticide fate models and their Use).

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CONTENTS

EXECUTIVE SUMMARY

What framework is recommended for estimating pesticide concentrations in soil?

A stepped approach is recommended.

Initially estimates should be made with simple models. But if these simple estimates are insufficient to demonstrate safety then more detailed simulation models should be used, and/or result from field studies if available. Details are given in Chapter 5.

What simple models are recommended?

Concentrations immediately after application.

The predicted environmental concentration in soil (PEC_S in mg/kg) immediately following a single application can be estimated as follows:

$$\text{Initial } PEC_S = A \times (1 - f_{int}) \; / \; (100 \times \text{depth} \times \text{bd})$$

where
A = application rate (g/ha)
f_{int} = fraction intercepted by crop canopy
depth = mixing depth (cm)
bd = dry soil bulk density (g/cm^3)

Assume a bulk density of 1.5 g/cm^3, and a mixing depth of 5cm for applications to the soil surface or 20cm where incorporation is involved. Unless better information is available the fraction intercepted is assumed to be 0 for applications to bare soil, or up to 0.5 for applications when a crop is present. Using these assumptions the concentration in soil immediately after a single application (mg/kg) becomes:

Initial PEC_S = $A / 750$ assuming no incorporation or interception
= $A / 3000$ assuming incorporation but no interception
= $A / 1500$ assuming no incorporation but 50% interception

$= A / 6000$ assuming incorporation and 50% interception

For multiple applications a simplifying worst-case assumption of additive soil residues could be made if this is sufficient to demonstrate safety. If first order dissipation can be assumed, then the concentration in soil immediately after n applications (in mg/kg), spaced i days apart is given by:

Initial PEC_S for n applications

$$= \text{Initial } PEC_S \text{ for 1 application} \times (1 - e^{-nki}) / (1 - e^{-ki})$$

where k is the dissipation rate constant given by:

$$k = \ln 2 / DT50$$

and DT50 = time for disappearance of half the chemical (days)

Generally laboratory transformation rates will be available at these early stages of the assessment process and should be used. If dissipation cannot be assumed to be first order then equivalent procedures can be used, or more detailed simulation models and/or field data can be used.

Time-weighted average concentrations

The time-weighted average concentration over a period of t days after application is given by:

$$\text{Average } PEC_S \text{ over t days} = \text{Initial } PEC_S \times (1 - e^{-kt}) / kt$$

(Currently the regulations require time-weighted average concentrations 1, 2 and 4 days after the last application, and also over 7, 28, 50 and 100 day periods where relevant.)

Long-term concentrations and build-up

If a pesticide is relatively persistent then concentrations in soil may build up and reach a plateau. Once the plateau has been reached concentrations fluctuate between a maximum when an application has just been made and a minimum just before the next application has been made. If first order dissipation of residues can be assumed then the time-weighted average concentration once the plateau has been reached is given by:

$$\text{Plateau average } PEC_S = \text{Initial } PEC_S \text{ for 1 application} / ki$$

whilst the maximum concentration during the plateau period, immediately after an application is given by:

$$\text{Plateau maximum } PEC_S = \text{Initial } PEC_S \text{ for 1 application } / (1 - e^{-ki})$$

If dissipation cannot be assumed to be first order then equivalent procedures can be used, or more detailed simulation models and/or field data can be used.

What more detailed simulation models are available and what is their validation status?

Models available

All leaching models previously reviewed by FOCUS could be used in principle. Some new versions of models previously examined are now available and have been reviewed (Chapter 2). Two additional models, relevant for PEC_S but not previously considered by the FOCUS Leaching Model Workgroup are also reviewed (BAM and PERSIST).

Their characteristics and validation status

With most pesticides, transformation in soil is the primary factor controlling persistence in the topsoil, so of the simulations models only ones which consider temperature and moisture effects on transformation justify detailed consideration, since in most cases only these are likely to offer significant improvements over the simple models described earlier. The models which consider temperature and moisture effects on transformation are VARLEACH, PESTLA, PESTRAS, LEACHP and PELMO. There are only small differences in the way the effect of temperature and moisture are mathematically considered in these models (moisture sensitivity in LEACHP is an exception). Their transformation routines are all based on or very similar to the model PERSIST, which is a set of transformation routines without any other loss mechanisms like leaching, volatilisation, plant uptake or runoff. Therefore it makes sense first to consider the validation status of PERSIST. The model PERSIST has been tested in numerous situations in the field, and with compounds that are not volatile or highly mobile it can give accurate predictions of soil residue levels. However it tends to overestimate soil residue levels in cases where other loss mechanisms are significant, eg volatilisation and leaching. In these cases, simulation models which use transformation routines similar to PERSIST and which include additional loss processes could be considered.

Validation has focused on transport processes rather than on predicting concentrations in the topsoil. The simulation models which consider temperature and moisture effects on transformation (VARLEACH, PESTLA/PESTRAS, LEACHP, MACRO and PELMO) all do so in a similar way to PERSIST and since transformation is generally the main loss process in topsoil, the choice of appropriate input parameters is expected to be more important than the choice of model in determining the results. The validation status of the additional loss processes included in these five simulation models is low with respect to their ability to predict concentrations in topsoil.

What is the role of field dissipation studies for estimating PEC values in soil?

For the first stage assessment of PEC values in soil it is appropriate to use laboratory transformation rates. And if more detailed simulation models are used, the main pesticide-related inputs are transformation rates derived from various laboratory studies. But field dissipation studies do have an important role to play, since they are a direct measure of concentrations in soil under field conditions. Field dissipation studies should, therefore, be considered more definitive than modelling predictions. However, the use of field data needs care to ensure that the results have predictive value. For example, if leaching of a highly mobile chemical significantly speeds dissipation on a very sandy soil, the resulting dissipation rate has limited value as an indicator of what will happen on fine-textured soils. Another restriction with respect to the use of field data is the soil temperature; if field persistence studies have been carried out at temperatures that are, for example, 10°C warmer than relevant, this may lead to interpretation problems.

If field dissipation is significantly faster than aerobic soil transformation rates in the lab, this may indicate that additional processes may be important in the field, eg photolysis, volatilisation. If this conclusion is supported by data specific to these processes (eg lab photolysis rates, vapour pressure) then it may be appropriate to use the field dissipation rates for the estimation of PEC values in soil. It is sometimes possible to support the use of the field data by eliminating the possibility that other dissipation routes were important in the field studies (eg eliminating runoff if the site was flat). Ideally, it may be possible to use detailed simulation models to show that the field results are consistent with lab-based estimates of rates of transformation, photolysis etc. However, this is often not possible, either because of incomplete characterisation of the field studies, or because of the inadequacy of some existing lab methods (some lab study designs are designed to demonstrate the existence of particular dissipation routes, not to produce numbers which can be used to predict field rates of the same process).

In any case, if field dissipation data exist, then they should be considered in the assessment. Field dissipation rates often differ from laboratory transformation rates, and the reasons are not always clear. The possibility that some laboratory studies are not predictive should also be considered, because of the difficulties of maintaining active microorganisms in the lab over long periods of time, and inadequacy of protocols followed, often decades ago. It could be argued that there is less to go wrong with field studies provided that an adequate soil sampling strategy is applied. Field dissipation studies also have particular value when the rate of transformation in the lab is too slow to determine with certainty in the laboratory.

What inputs should be used to characterise the effects of temperature and moisture on transformation?

Effect of temperature

Models vary according to whether activation energy or a Q_{10} value is required as input. A distribution of activation energies and Q_{10} values have been derived from extensive measurements. The average activation energy found was 54000 J mole^{-1} , which is equivalent to a Q_{10} value of 2.2. This means that for each 10°C change in temperature the DT50 will change by a factor of 2.2. Variation in measurements of Q_{10} for individual pesticides are as great as variations between pesticides, which indicates that little information would be added by measuring Q_{10} values as opposed to estimating them.

Effect of moisture

All the models considered which allow for moisture effects on transformation (except LEACHP), do so using the same equation which relates transformation rate to water content (in PESTRAS this is combined with another equation, resulting in a relationship between transformation rate and water tension).

$$DT50 = A\, M^{-B}$$ (DT50 is the half-life, M is soil moisture content, and A and B are constants)

There is one parameter which affects the relationship in this equation, usually represented by the letter B. An average value for B of +0.8 is recommended (Doctoral thesis of B. Gottesburen, “Konzeption, Entwicklung und Validierung des wissensbasierten Herbizid-Beratungssystems HERBASYS”, 1991). Variation in measurements of B for individual pesticides are as great as variations between pesticides, indicating that little information would be added by measuring B values as opposed to estimating them. LEACHP contains its own unique relationship between transformation rate and soil water potential.

What scenarios are available for use in simulation models?

Scenarios of crop, soil and weather data are needed not just for estimating concentrations of pesticides in soil, but also for leaching and other fate and exposure assessments. These scenarios should be accessible to all and should cover the whole EU. The scenarios should also exist in the form of input datasets suitable for use in the various simulation models. This would ensure consistency of assessment methods.

Some work was done as part of the FOCUS Leaching Model Workgroup activities (Leaching models and EU registration, EU Document DOC.4952/VI/95) and this is developed further in this report. In principle there are several possible starting points for developing scenarios, bearing in mind that the aim is to only have about 10 in total. One is to pick 10 major crops and examine the soils and climate where they are grown. An alternative is to examine climate, classify this into about 10 classes, and examine the soils and crops grown in climatic area. The latter approach is the one which has been taken here. In fact 8 climatic areas are identified, and for each of these some basic soil and cropping data is presented.

The level of detail and quality of data is not ideal, and better data exists. Unfortunately access to the best datasets is restricted - this problem needs to be addressed. Further work is also needed to test the representativeness of the scenarios, and to develop them into model input datasets.

What improvements are needed?

With most pesticides, transformation in soil is the primary factor controlling persistence in the topsoil, and this has been satisfactorily dealt with both in terms of data available and modelling. Leaching and macropore flow are important for transport to groundwater but relatively unimportant for predicting topsoil concentrations of pesticides, and have been satisfactorily dealt with for this purpose. Other factors which are important, and on which more work is needed are volatilisation and photolysis. Although laboratory measurements of pesticide properties relevant to these factors are currently made, to some extent there is not general agreement about how to use these data in models, and to some extent there are inadequate field data to validate the routines which have been incorporated into the models. Interception of sprayed pesticide by the crop canopy is also an important factor, but insufficient information is available to guide model assumptions.

As well as the scientific process issues described above, there are two other significant improvements which are needed in order to support the satisfactory use of simulation models in the EU regulatory process. The first improvement is that simulation models to be used at the EU level need also to be institutionalised and maintained at the EU level. This involves a nominated institution being responsible for version control, code quality, user support, manuals, training and a register of users. This need was also identified by the FOCUS Leaching Model Workgroup, and applies to all simulation models to be used in regulatory decision-making. The second improvement is the open provision of a full set of crop, soil and weather scenarios representing the whole EU. This need was highlighted by the FOCUS Leaching Model Workgroup, and further progress has been made by the current group. However more work is needed before the goal of a full set of accessible scenarios has been achieved.

Does an agreed method exist for estimating transformation rates at 10°C from measurements made at 20°C?

Yes

A distribution of activation energies and Q_{10} values have been derived from extensive measurements. The average activation energy from this distribution is equivalent to a Q_{10} value of 2.2, which means that the DT50 at 20°C should be multiplied by 2.2 to give a best estimate of the DT50 at 10°C. From the distribution of Q_{10} values 90th and 95th percentiles have also been derived, which would lead to longer, worst-case DT50 estimates. Variation in measurements of the temperature-sensitivity of transformation rates for individual pesticides are as great as variations between pesticides, which indicates that little information would be added by measuring as opposed to estimating transformation rates at 10°C. Some debate still continues as to the suitability of these Q_{10} values for countries where average temperatures may be lower than 10°C but at present no solutions are available to the problem.

Chapter 1

Temperature and pesticide transformation

A. Walker, A. Helweg and O-S. Jacobsen

One component of Annex II to Directive 91/414/EEC concerns the concept of extrapolation of laboratory-derived transformation data from 20 to 10°C. A relationship that could be used for this purpose is the Arrhenius Equation. There are numerous reports in the literature of the use of this relationship to describe temperature dependence of transformation in soil, and it has the form:

$$k = A_o \exp[-(E_a/RT)] \tag{1.1}$$

where k is the rate constant for transformation (day^{-1}), E_a is the activation energy (J mol^{-1}), R is the gas constant (J mol^{-1} K^{-1}), T is the temperature (K) and A_o is a constant.

With first-order reaction kinetics (assumed in most models), the rate constant k and half-life (DT50, days) are interchangeable according to:

$$k = \ln 2/DT50 \tag{1.2}$$

and an alternative form of equation 1 becomes:

$$DT50_s = DT50 \exp[(E_a/R)(1/T_s - 1/T)] \tag{1.3}$$

where $DT50_s$ and DT50 are half-lives at temperatures T_s (reference) and T respectively.

An alternative way to express the effects of temperature on transformation that derives from the Arrhenius relationship is to use the Q_{10}-value. This is defined as the change in rate for a 10°C change in temperature, and is particularly relevant to the extrapolation of data from 20 to 10°C. With a base temperature of 20°C, the relationship between Q_{10} and E_a (Equations 1 and 3) is:

$$Q_{10} = \exp[E_a/68627] \tag{1.4}$$

Experimental data on temperature effects

The Arrhenius equation has been widely used to evaluate temperature effects on transformation, and it is clearly a validated routine for use in this context. Although there are limits to the range of temperatures over which the relationship will be accurate, virtually all of the experimental data from which activation energies have been derived do include rate measurements covering the range from 10 and 20^{o}C. There is considerable variability in the calculated values for the activation energy. A brief survey of the literature has located 148 values for this parameter (23 of which were reported in the review of Hamaker (1971), and 93 in the review of Gottesbüren (1991)). The additional 32 values have been published more recently or are unpublished data derived from studies at HRI, Wellesbourne, UK. Some of the activation energies reported in the reviews of Hamaker and Gottesbüren are summarised in Table 1. These data indicate that it may be possible to estimate a reasonably good correlation factor between soil temperature and transformation rate, at least compared with that possible between transformation and other parameters such as soil type, microbial activity, moisture etc. Another observation from the data in Table 1 is that the mean activation energy does not vary much from one compound to another which suggests that the overall variability may reflect errors in individual determinations. All of the data in Table 1 plus the additional information from more recent studies are summarised in Figure 1. These same data are plotted in an alternative format in Figure 2 where the cumulative percentage of the total number of observations is plotted as a function of the Q_{10}-value. The data provide a mean activation energy of 54.0 kJ mole^{-1}, which translates to a Q_{10} of 2.20. The coefficient of variation in E_a-values was about 48%. The ninety percentile value of Q_{10} derived from the data was 2.77. Whereas the ninety five percentile value is about 3.1.

For maleic hydrazide in Table 1 the rate of transformation was determined by evolution of $^{14}CO_2$ from ^{14}C-labelled herbicide and the E_a value is relatively high compared to the other data in the Table. This is presumably because mineralisation may well involve a complex sequence of rate processes whereas loss of parent compound will involve just a single step. When considering loss of parent compound and extrapolation of data from 20 to 10^{o}C, then the Q_{10} values mentioned above will be most appropriate. A much higher value would be needed if total mineralisation was to be considered.

Conclusion

The Arrhenius equation is a validated relationship which can be used to describe temperature effects on transformation. A Q_{10}-value of 2.20 could reasonably be used to extrapolate DT_{50} data derived at 20^{o}C to expected values at 10^{o}C, since this is the mean value derived from over 140 individual studies. If a more conservative estimate was required a larger Q_{10}-value would be required. A value of 2.77 would give a 90% probability of encompassing the true half-life at the lower temperature, while a Q_{10}-value of 3.1 would be necessary to ensure that the correlation covered 95% of the cases.

Figure 1.: Frequency distribution of activation energies (148 observations).

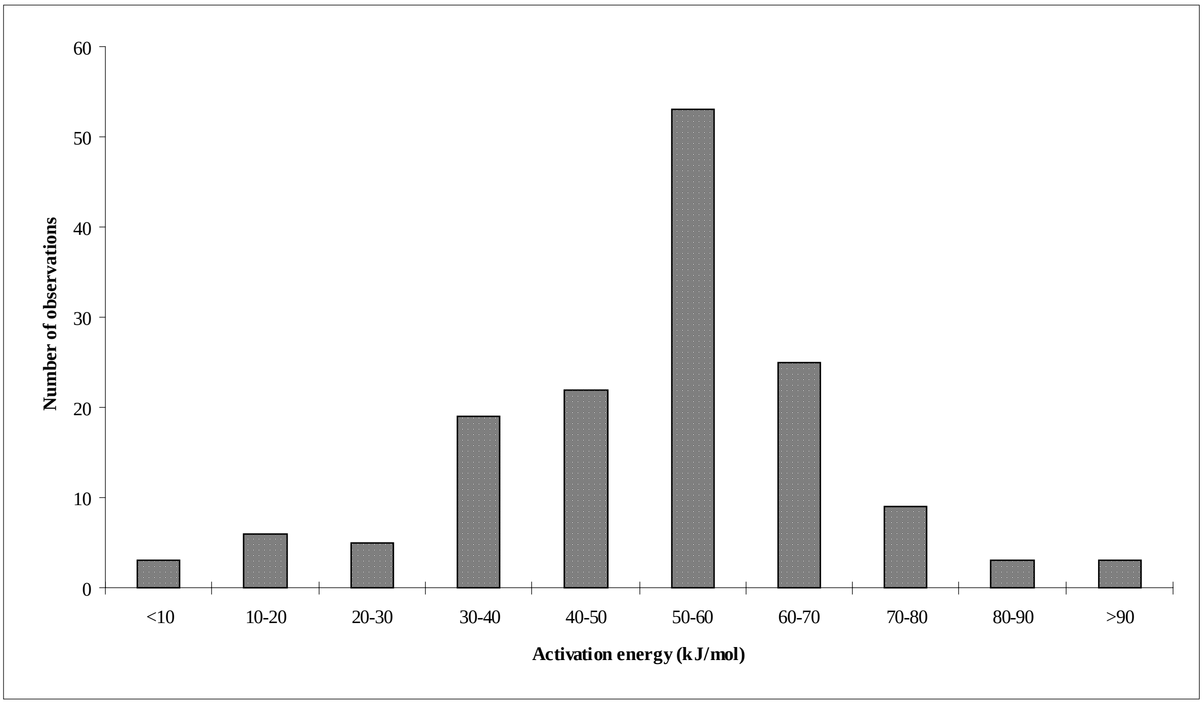

Figure 2.: Cumulative percentage distribution of Q10-values.

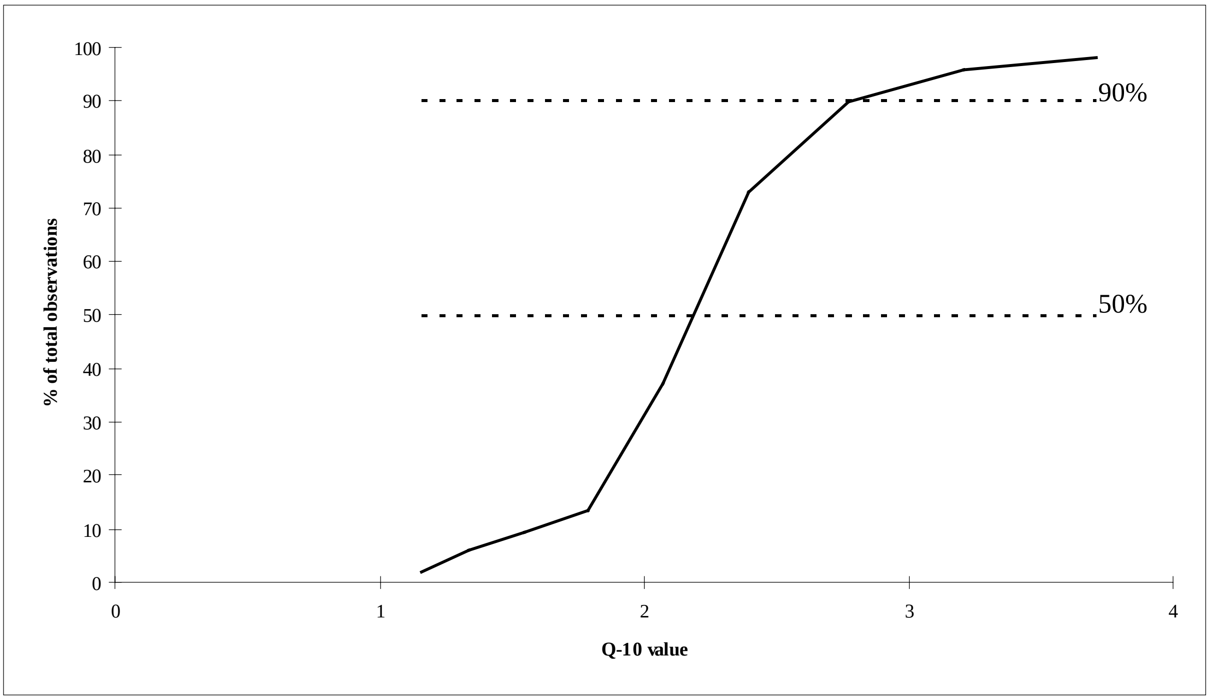

Table 1. Activation energy values for herbicides from thesis of Gottesbüren (1991). Supplemented with data from Helweg (1981) and Hamaker (1972) where referred to.

Herbicide	E_a (kJ mol^{-1})	Reference
2,4,5-T	85.1	Walker & Smith (1979)
Alachlor	57.0	Walker & Brown (1985)
Ametryne	5.9	Hamaker (1972)
Amitrole	26.1	Hamaker (1972)
	12.8	Hamaker (1972)
Mean 19.5		
SD 9.4		
SD% 48.4 %		
Atrazine	69.9	Walker (1978)
	50.6	Walker & Zimdahl (1981)
	51.1	Walker & Zimdahl (1981)
	45.4	Walker & Zimdahl (1981)
	48.8	Haigh & Ferris (1991)
	43.5	Smith & Walker (1989)
	75.0	Hamaker (1972)
Mean 54.9		
SD 12.4		
SD% 22.5 %		
Bromacil	89.2	Hamaker (1972)
Chlorthaldimethyl	92.0	Walker (1978)
Chloroxuron	44.1	Hamaker (1972)
Chlorsulfuron	66.6	Walker & Brown (1983)
Chlortoluron	41.7	Pestemer
	33.1	(1983,unpublished)
	61.4	Düfer (1991)
	51.2	Düfer (1991)
Mean 46.9		Düfer (1991)
SD 12.2		
SD% 26.0 %		
Cyanazine	60.6	
		Smith & Walker (1989)
Dimethachlor	57.0	
		Walker & Brown (1985)

Table 1. Cont.

Herbicide	E_a (kJ mol^{-1})	Reference
Diuron	32.8	Hamaker (1972)
	7.9	Hamaker (1972)
Mean 20.4		
SD 17.6		
SD% 86.5 %		
Ethofumesate	38.8	Laboratory experiments (1987)
	49.8	
	54.1	Laboratory experiments (1990)
	58.0	
	18.0	Laboratory experiments (1990)
Mean 43.7		
SD 16.1		Laboratory experiments (1990)
SD% 36.8 %		
		Parameter estimation (1989)
Fenuron	6.2	
Isoproturon	47.4	
	51.4	
	41.8	Hamaker (1972)
	39.8	
	45.3	Pestemer (1985, unpublished)
	55.4	
	41.9	Walker (pers. comm.)
	58.8	Mudd et al. (1983)
Mean 47.7		Berger (1989)
SD 6.9		Berger (1989)
SD% 14.4 %		Blair et al. (1990)
		Blair et al. (1990)
Isoxaben	47.1	Blair et al. (1990)
Linuron	28.8	
	37.4	
	35.9	
	51.6	Walker (1987)
	49.0	
	39.0	Walker (1978)
Mean 40.3		Walker & Zimdahl (1981)
SD 8.5		Walker & Zimdahl (1981)
		Walker (1987)

SD% 21.2 %		Usoroh & Hance (1974) Hamaker (1972)

Table 1. Cont.

Herbicide	Parameter E_a (kJ mol^{-1})	Reference
Maleic hydrazide	60.0	Helweg (1981)
	78.0	Helweg (1981)
	96.0	Helweg (1981)
Mean 78.0		
SD 18.0		
SD% 23.1 %		
Metamitron	46.6	Walker & Bond (1978)
	56.0	Bunte (1991)
	65.8	Bunte (1991)
	38.4	Bunte (1991)
Mean 51.7		
SD 11.8		
SD% 22.9 %		
Metazachlor	60.8	Walker & Brown (1985)
Methabenzthiazuron	123.0	Pestemer & Auspurg (1987)
	54.0	Bunte (1991)
	35.6	Bunte (1991)
	46.9	Laboratory Experiments (1988)
Mean 64.9		
SD 39.5		
SD% 60.9 %		
Metolachlor	49.5	
	44.3	Walker & Zimdahl (1981)
	51.6	Walker & Zimdahl (1981)
	52.0	Walker & Zimdahl (1981)
Mean 49.4		Walker & Brown (1985)
SD 3.5		
SD% 7.2 %		
Metribuzin		
	55.0	
	65.0	Pestemer & Auspurg (1987)
Mean 59.8	59.4	Walker (1978)
SD 5.0		Smith & Walker (1989)

SD% 8.4 %		

Table 1. Cont.

Herbicide	E_a (kJ/mol^{-1})	Reference
Metsulfuron-methyl	69.4	Calculated from Günther (1991)
Monolinuron	132.8	
		Hamaker (1972)
Monuron	31.9	
		Hamaker (1972)
Napropamide	32.6	
	55.6	Walker (1974)
		Walker (1987)
Pendimethalin	51.8	
		Calculated from Walker & Bond (1977)
	53.9	
	167.0	
Mean 90.9		Laboratory experiments (1987)
SD 65.9		
SD% 72.5 %		Parameter estimation (1989)
Phenmedipham	73.6	
Prometryne	56.1	
		Pestemer (1987, unpublished)
Propachlor	57.1	
Propyzamide	61.7	Walker (1976 a)
	60.4	
	71.9	Walker & Brown (1985)
	70.1	
	63.3	Walker (1976 b)
	61.3	Walker (1976 b)
	74.6	Walker (1976 b)
	53.6	Walker (1976 b)
Mean 64.6		Walker (1976 b)
SD 7.0		Pestemer (1986, unpublished)
SD% 10.8 %		
		Walker (1978)
		Walker (1987)

Table 1. Cont.

Herbicide	E_a (KJ/mol^{-1})	Reference
Simazine	61.5	Walker (1976 a)
	50.0	Walker et al. (1983)
	45.0	Walker et al. (1983)
	56.0	Walker et al. (1983)
	39.0	Walker et al. (1983)
	58.0	Walker et al. (1983)
	56.0	Walker et al. (1983)
	27.0	Walker et al. (1983)
	51.0	Walker et al. (1983)
	45.0	Walker et al. (1983)
	35.0	Walker et al. (1983)
	34.0	Walker et al. (1983)
	69.0	Walker et al. (1983)
	64.0	Walker et al. (1983)
	35.0	Walker et al. (1983)
	45.0	Walker et al. (1983)
	69.5	Walker (1978)
	49.6	Bunte (1991)
	55.0	Bunte (1991)
	34.4	Bunte (1991)
	27.2	Bunte (1991)
	54.5	Hamaker (1972)
	70.0	Hamaker (1972)
	61.6	Hamaker (1972)
Mean 47.7 SD 13.2 SD% 26.5 %		

Table 1. Cont.

Herbicide	E_a (kJ mol^{-1})	Reference
Terbacil	36.1	Hamaker (1972)
Terbuthylazine	52.4	Parameter estimation (1990)
	51.0	Parameter estimation (1990)
	52.4	Parameter estimation (1990)
Mean 51.9		
SD 0.8		
SD% 1.6 %		
Triallate	40.1	Laboratory experiments (1987)
	37.6	Laboratory experiments (1987)
Mean 38.9		
SD 1.8		
SD% 4.6 %		
Trifluralin	52.5	Walker (1978)
Number of measurements	114	
Arithmetic mean	54.12	
Standard deviation	21.90	
Standard deviation (%)	40.5	

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Chapter 2

Assessment of models for PEC_{soil} calculation

H. Schäfer, R. Jones, A. Walker, K. Travis

This section is intended to give an overview over models, which seem to be appropriate for calculating PEC_{soil}.

Generally all simulation models, which are used for the estimation of the leaching behaviour of a compound should also be able to give an estimate of PEC_{soil}. These models have already been assessed by the FOCUS Leaching Models Working Group (J. Boesten et al., 1995). Since the end of this work the models PRZM-2, PESTLA/PESTRAS and PELMO have been updated. While most of the assessment done by Leaching Models Working Group is still valid, the improvements of these three models will be reported below and should replace the respective sections of the former assessment.

Some additional models have been identified, which might be appropriate. These models are: BAM, PERSIST, FUGACITY and some simple models, which are based on a single equation. The latter ones are: EFATE , TWA (time weighted average), first order residue build-up, Dutch build-up model, BBA routines.

Updated Models:

PRZM-2:

1. General information

Most recent release:	Release 2.0
Date of most recent release:	Oct., 1994

3. Model science
3.2 Numerical technique

Space increments: set by user;
The 'mixing depth' used for surface-applied chemicals and for extraction by runoff is set either to 1 cm or depth of surface compartment, whichever is greater.
Soil moisture averaging depth is set to 10 cm or depth of surface compartment, whichever is greater.

PESTLA/PESTRAS

The most recent release of PESTLA is version 2.3, which was assessed by the FOCUS Leaching Models Working Group. PESTRAS is based on PESTLA 2.3, but contains two major extension. Firstly routines for the simulation of metabolites were added and secondly it has the capability of taking into account pesticide volatilisation. Therefore, the respective paragraphs in section 3.5 of the model assessment chapter of the Leaching Models Working Group report should be updated. In the near future both models will be combined into one model with a new name (not yet defined). A complete assessment of this version is under preparation for the report of the Surface Water Modelling Working Group.

PELMO

1.	General information	
	Most recent release:	Release 2.01
	Date of most recent release:	May, 1995
2.1	User manual	
	Language:	German and English
2.5	Input/Pre-processor	
	User friendliness:	Medium
	Help Utility	Yes
	Databases included:	German standard scenarios for weather and soil Database for phenological data of major crops
3.5	Pesticide model	
	Sorption	
	Type of model:	Freundlich isotherm and/or increasing with time
	Dependency on environmental factors:	Kd specified for each horizon or Koc specified along with organic carbon for each horizon; Kd may depend on pH (calculation based on value)
	Transformation in soil	
	Type of model:	First order kinetics
	Volatility:	Volatility across soil surface using Henry's law

Simple PEC_S calculations assuming first order dissipation.

If an assumption of first order decline of soil residues levels is made, and EU guidance on other assumptions is followed, then the following general relationships apply for estimating concentrations of pesticides in soil.

The concentration in soil (mg/kg) immediately after a single application of a pesticide is given by:

$$\text{Initial } PEC_S = A \text{ x } (1- f_{int}) \;/\; (100 \text{ x } depth \text{ x } bd) \tag{2.1}$$

where: PEC_S is the predicted environmental concentration in soil (mg/kg)
A = application rate (g/ha)
f_{int} = fraction intercepted by crop canopy
depth = mixing depth (cm)
bd = dry soil bulk density (g/cm^3)

EU guidance is to assume a bulk density of 1.5 g/cm^3, and a mixing depth of 5cm for applications to the soil surface or 20cm where incorporation is involved. Unless better information is available the fraction intercepted is assumed to be 0 for applications to bare soil, or up to 0.5 for applications when a crop is present. Using these assumptions the concentration in soil immediately after a single application (mg/kg) becomes:

$\text{Initial } PEC_S = A / 750$ assuming no incorporation or interception
$= A / 3000$ assuming incorporation but no interception
$= A / 1500$ assuming no incorporation but 50% interception
$= A / 6000$ assuming incorporation and 50% interception

Assuming first order dissipation, the concentration in soil at a particular point in time t days after application is given by:

$$PEC_S \text{ at time } t = \text{Initial } PEC_S \text{ x } e^{-kt} \tag{2.2}$$

where k is the dissipation rate constant given by:

$$k = 0.693 / DT50$$

and DT50 = time for disappearance of half the chemical (days)

The time-weighted average concentration over period of t days after application is given by:

$$\text{Average } PEC_S \text{ over } t \text{ days} = \text{Initial } PEC_S \times (1 - e^{-kt}) / kt \qquad (2.3)$$

The concentration in soil immediately after n applications (in mg/kg), spaced i days apart is given by:

$$\text{Initial } PEC_S \text{ for } n \text{ applications} = \text{Initial } PEC_S \text{ for 1 application} \times (1 - e^{-nki}) / (1 - e^{-ki}) \qquad (2.4)$$

With applications spaced i days apart, ultimately a plateau will be reached. Once the plateau has been reached concentrations fluctuate between a maximum when an application has just been made and a minimum just before the next application has been made. The time-weighted average concentration once the plateau has been reached is given by:

$$\text{Plateau average } PEC_S = \text{Initial } PEC_S \text{ for 1 application} / ki \qquad (2.5)$$

whilst the maximum concentration during the plateau period, immediately after an application is given by:

$$\text{Plateau maximum } PEC_S = \text{Initial } PEC_S \text{ for 1 application} / (1 - e^{-ki}) \qquad (2.6)$$

Equations 2.1 and 2.2 described above have been implimented in a number of different ways by researchers to satisfy different needs. This has generally been done in spreadsheets and a number of these applications are described below:

TWA

Author:	R. Grau & H. Schäfer
Responsible institution:	BAYER
Published:	No
Model science:	single compartment model lumped first order transformation rate multiple applications
Required input:	DT50, application rate and frequency
Model output:	Concentration as function of time and time weighted concentration as function of time

for single application:

$$\frac{\bar{c}}{c_o} = \frac{DT50}{\Delta t \cdot \ln 2}\left(1 - \exp\left\{-\frac{DT50}{\Delta t \cdot \ln 2}\right\}\right) \qquad (2.7)$$

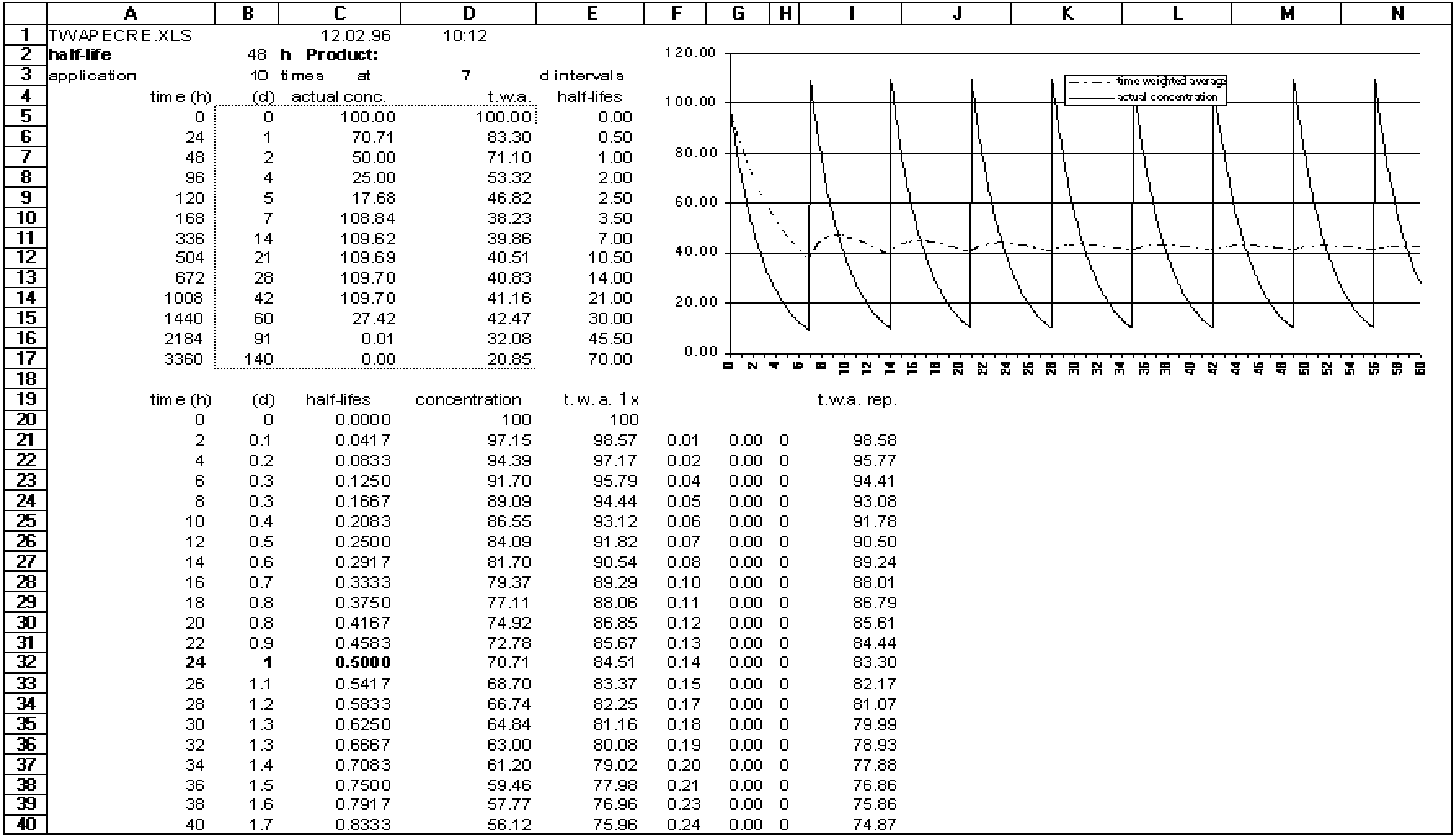
$\bar{c}$ = time weighted average concentration
c_o = initial concentration
Δt = time interval

for multiple application:
TWA for multiple applications was developed as an EXCEL sheet. As input the total number of applications, the application interval and a half-life, representative for the compartment under investigation, is needed. Figure 1 shows an example for a compound which is applied 10 times every 7th day and has a half-life of 48 h. Additionally to a tabular listing of the results a graphical representation is given.

First order residue build-up

Author:	R. Jones
Responsible institution:	Rhone Poulenc
Published:	No
Model science:	single compartment model lumped first order transformation rate single application per simulated year
Required input:	DT50
Model output:	Concentration expressed as percent of applied amount as function of time
Example calculation	Figure 2 shows an example calculation of the build up model.

Figure 1



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	TWAPECRE.XLS		12.02.96	10:12										
2	**half-life**	48	**h Product:**											
3	application	10	times at	7	d intervals									
4	time (h)	(d)	actual conc.	t.w.a.	half-lifes									
5	0	0	100.00	100.00	0.00									
6	24	1	70.71	83.30	0.50									
7	48	2	50.00	71.10	1.00									
8	96	4	25.00	53.32	2.00									
9	120	5	17.68	46.82	2.50									
10	168	7	108.84	38.23	3.50									
11	336	14	109.62	39.86	7.00									
12	504	21	109.69	40.51	10.50									
13	672	28	109.70	40.83	14.00									
14	1008	42	109.70	41.16	21.00									
15	1440	60	27.42	42.47	30.00									
16	2184	91	0.01	32.08	45.50									
17	3360	140	0.00	20.85	70.00									
18														
19	time (h)	(d)	half-lifes	concentration	t.w.a. 1x				t.w.a. rep.					
20	0	0	0.0000	100	100									
21	2	0.1	0.0417	97.15	98.57	0.01	0.00	0	98.58					
22	4	0.2	0.0833	94.39	97.17	0.02	0.00	0	95.77					
23	6	0.3	0.1250	91.70	95.79	0.04	0.00	0	94.41					
24	8	0.3	0.1667	89.09	94.44	0.05	0.00	0	93.08					
25	10	0.4	0.2083	86.55	93.12	0.06	0.00	0	91.78					
26	12	0.5	0.2500	84.09	91.82	0.07	0.00	0	90.50					
27	14	0.6	0.2917	81.70	90.54	0.08	0.00	0	89.24					
28	16	0.7	0.3333	79.37	89.29	0.10	0.00	0	88.01					
29	18	0.8	0.3750	77.11	88.06	0.11	0.00	0	86.79					
30	20	0.8	0.4167	74.92	86.85	0.12	0.00	0	85.61					
31	22	0.9	0.4583	72.78	85.67	0.13	0.00	0	84.44					
32	**24**	**1**	**0.5000**	70.71	84.51	0.14	0.00	0	83.30					
33	26	1.1	0.5417	68.70	83.37	0.15	0.00	0	82.17					
34	28	1.2	0.5833	66.74	82.25	0.17	0.00	0	81.07					
35	30	1.3	0.6250	64.84	81.16	0.18	0.00	0	79.99					
36	32	1.3	0.6667	63.00	80.08	0.19	0.00	0	78.93					
37	34	1.4	0.7083	61.20	79.02	0.20	0.00	0	77.88					
38	36	1.5	0.7500	59.46	77.98	0.21	0.00	0	76.86					
39	38	1.6	0.7917	57.77	76.96	0.23	0.00	0	75.86					
40	40	1.7	0.8333	56.12	75.96	0.24	0.00	0	74.87					

Figure 2.
FIRST ORDER RESIDUE BUILDUP IN SOIL

Assumptions

first order kinetics
no losses due to runoff, leaching, or volatilization
annual applications at the same date

Model

A(1) = 100

A(1) is the amount remaining immediately after initial application
(expressed as a percent of the yearly application)

D = EXP(-LN(2)/(HF/12))

D is the fraction of the material present immediately after an application that is not degraded during the year before the next application
HF is the half-life in months

A(t) = A(t-1)*D + 100

A(t) is the amount of material remaining after the application in year t
(expressed as a percent of the yearly application)

Half-life = 9 months

D = 0.39685

Year	A(t)
1	100.00
2	139.69
3	155.43
4	161.68
5	164.16
6	165.15
7	165.54
8	165.69
9	165.76
10	165.78
11	165.79
12	165.79
13	165.80
14	165.80
15	165.80
16	165.80
17	165.80
18	165.80
19	165.80
20	165.80
21	165.80
22	165.80
23	165.80
24	165.80
25	165.80

Dutch build-up model:

Author: J. Hamaker
Responsible institution:
Published: Advances in Chemistry, 1966, 60, 122-131
Model science: single compartment model
lumped first order transformation rate
Required input: DT50
Model output: Concentration expressed as percent of applied amount as function of time

$$
\begin{aligned}
&\log\frac{c_o}{c} = \frac{0.30103\cdot t}{t_{1/2}}\\
&f = {}^{c}\!/_{c_o}\\
&\frac{r}{c_o} = 1 + f_1 + f_1^{\,2} + \ldots + f_1^{\,n-1}
\end{aligned}
\qquad (2.8)
$$

c_o = initial concentration
c = concentration at time t
f_1 = fraction left after one year
$t_{1/2}$ = half life of decomposition
r = accumulated residue, immediately after addition of annual increment
n = number of applications

BBA routines:

Author:
Responsible institution: BBA
Published: No
Model science: single compartment model
multiple application
transformation not explicitly considered
calculations are based on constant mixing depth of 5 cm and soil bulk density of 1.4 g/ml
Required input: application rate
Model output: Initial concentration and concentration after repeated application

$$PEC = rate \cdot 1.43 \cdot (1 - f_B) \cdot [1 + f_S(n-1)] \qquad (2.9)$$

PEC in mg/kg
rate in kg/ha
f_B = 0 for soil without plant cover or soil with low plant cover and grassland
f_B = 0.5 for soil with plant
f_S = 0.5 for DT90 < 100 days (lab)
f_S = 1 for DT90 > 100 days (lab)
n = number of applications

EFATE

Author:	R. Lee
Responsible institution:	U.S. EPA
Published:	No
Model science:	single compartment model lumped first order transformation rate multiple applications
Required input:	DT50, application rate and frequency
Model output:	Concentration as function of time and mean concentration

Simulation Models:

1 General Information		
Name of model	**BAM**	**Pesticide Persistence Program**
Name or number of most recent release	**B**ehaviour **A**ssessment **M**odel	PERSIST
Intended use of model	Screening of transport and loss in soil	Calculation of pesticide dissipation in soil
Model developers	W.A. Jury, W.F. Fischer, W.J. Farmer	A. Walker, A. Barnes
Sponsoring institution		
Date of most recent release		June 1991

2.1 User manual		
Availability	not available	not available
Language		
Clarity		
Defines model limitations		
Includes conceptual model description		
Includes mathematical model description		
Includes sensitivity analysis		
Provides assistance in determining model parameters		
Provides references		

2.2 Other documentation considerations		
Tightness of version control		no control
Availability of source code		available

2.3 System considerations		
Hardware requirements		80286 or higher, DOS
Run time for standard scenario		low
Reliability		high
Clarity of error messages		no messages

2.4 Support		
Method of support		
Availability of information about bugs and corrections		
Training for users		

2.5	**Input/Pre-processor**		
	User friendliness		interactive input
	Help utility		none
	Data range checking		no
	Sample input file		sample weather data file included
	Database included		no
	Availability of needed data		available
	Flexibility		low

2.6	**Output/Post-processor**		
	Nature of output		tabular
	User friendliness		low
	Help utility		no
	Sample file		none
	Flexibility		low
	Documents input parameters		no
	Clarity of output reports		low

3.1	**Compartments considered**	soil (soil, soil water, soil air)	soil

3.2	**Numerical technique**	analytical solution	
	Adequacy of algorithm	n.a.	
	Definition of hydrodynamic lower boundary conditions	n.a.	
	Stability	n.a.	
	Numerical dispersion	n.a.	
	Time increments	n.a.	
	Space increments	n.a.	
	Verification of numerical technique	n.a.	

3.3	**Soil model**	continuum model	1 homogeneous layer

3.4	**Hydrology model**		
	Type	steady flow (input)	water balance
	Evapotranspiration model	only evaporation considered steady flow (input)	Linacre or input
	Capillary rise	no	no
	Runoff and erosion	no	no
	Preferential flow	no	no

3.5	**Pesticide model**		
	Metabolites	no	no
	Sorption		no adsorption model
	Type of model	linear	
	Dependency on environmental parameters	function of organic carbon	

Transformation in soil		
Type of model	first order	first order
Dependency on environmental parameters	none	function of temperature and moisture
Mechanisms considered	only one transformation process considered	only one transformation process considered
Compartments considered	soil	soil
Dispersion in soil	yes	no
Volatility	considered	no
Plant uptake	no	no
Transformation on plant surfaces	no	no
Foliar washoff	no	no
Runoff and erosion	no	no

3.6 Agronomy model	none	none
Cultivation		
Irrigation		
Application		
Frequency of applications		
Application technique		

3.7 Plant model	none	none
Foliage		
Purpose		
Description		
Flexibility		
Rooting depth		
Purpose		
Description		
Flexibility		

3.8 Heat model	none	
Purpose		correction of transformation rate
Description		empirical correlation with air temperature

Evaluation:

All simple models should be addressed as screening models. As major processes, which may be of importance for the environmental behaviour of a pesticide, such as distribution between soil and crop, volatilisation, leaching etc. are not included in these models they tend to overestimate the concentration in the uppermost soil layer.
Some of these shortcomings are also true for the simulation models BAM (no plant model) and PERSIST (no plant model, no leaching, no volatilisation). A major drawback of these models is also that user manuals are not available.

Therefore, if more realistic estimation of the PEC_{soil} is needed, simulation models such as VARLEACH, PESTLA, LEACHP, PELMO or PRZM might be more appropriate. The higher input data demand of these models will be outweighed by their ability to describe pesticide behaviour and the environmental boundary conditions in more detail, leading to more realistic estimations. However, there are still important limitations. VARLEACH, for example, suffers from the same disadvantage as PERSIST in that no user manual is available and it does not include important loss processes such as volatilisation, and PRZM is of limited use because it does not include subroutines to calculate the effects of variations in soil moisture and temperature on rates of loss.

With most pesticides, transformation in soil is the major process controlling persistence in the plough layer. The five main simulation models of pesticide fate that incorporate sub-routines to simulate the effects of variable temperature and soil moisture on rates of transformation are (1) VARLEACH (Walker, 1987; Walker and Hollis, 1994) which incorporates the pesticide transformation model PERSIST first described by Walker and Barnes (1981), (2) PESTLA (Boesten and Van der Linden, 1991), (3) the most recent version of LEACHP (Hutson and Wagenet, 1992), (4) MACRO (Jarvis 1991) and (5) PELMO (Klein, 1995).

All of the models assume simple first-order kinetics of transformation, and most laboratory data at least approximate to these kinetics. They also assume that the effects of temperature and soil moisture variations on transformation rate are totally independent, and there is limited laboratory evidence to support this assumption (see for example Walker, 1976; 1978).

Transformation routines used in existing simulation models

Routines used in PERSIST and VARLEACH

The effects of moisture and temperature on transformation in the sub-routines of these models are taken into account by two sequential equations:

$$DT50 = A\ M^{-B} \qquad (2.10)$$

where DT50 is the half-life at a standard reference temperature, T, with soil moisture content M, and A and B are constants.

Temperature effects are then defined by a modified form of the Arrhenius relationship:

$$DT50_s = DT50 \exp[(E_a/R)\ (1/T_s - 1/T)] \qquad (2.11)$$

where $DT50_s$ is the half-life at soil temperature T_s, R is the gas constant (J mol^{-1} K^{-1}) and E_a is the activation energy. All temperatures are in K.

The first order rate constant (k, day^{-1}) is then calculated from $DT50_s$ by:

$$k = 0.693/DT50_s \qquad (2.12)$$

In all of these models, soil moisture is constrained to a maximum of field capacity (matric potential -5 kPa), and it is assumed that transformation ceases if soil temperature falls below 0^{o}C.

Routines used in PELMO

PELMO uses the same function for the effect of soil moisture on transformation as PERSIST and VARLEACH. The influence of soil temperature is described with the Q_{10}-formula:

$$DT50 = DT50_s\ Q_{10}^{(T - Ts)/10} \qquad (2.13)$$

where $DT50_s$ is the half-life at soil temperature T_s and Q_{10} is a constant. All temperatures are in °C. It is assumed that transformation ceases if soil temperature falls below 0^{o}C.

Routines used in PESTLA

PESTLA uses an almost identical sequence of relationships to that described above and defines the rate constant for transformation (k) by:

$$k = f_T \, f_M \, f_Z \, k_{ref} \qquad (2.14)$$

where k_{ref} is the rate constant at a reference temperature and soil moisture content, and the factors f_T, f_M and f_Z are appropriate corrections for variations in temperature, soil moisture content and depth in the soil profile respectively. Moisture and temperature corrections are made using modified forms of relationships 2.10 and 2.11 above. Where the temperature corrections are concerned:

$$f_T = \exp[\{E_a/(R\ T\ T_S)\}\ (T - T_S)] \qquad (2.15)$$

which is derived directly from equation 2.11 above.

Routines used in LEACHP

Moisture effects on transformation are described by a sequence of linear relationships between the first-order rate constant and soil water potential. A minimum soil water potential is specified below which there is zero transformation. The rate constant increases linearly with soil water potential from this minimum to an optimum value (Note that the soil water potential is negative in soil and that an increase of this potential implies that the soil becomes wetter). The rate remains at the optimum until an upper limiting value of soil water potential is reached and then decreases linearly to water saturation where the rate is set to a predetermined proportion of the optimum rate. The various points along this sequence of relationships are specified by the model user.

Temperature effects are simulated using a Q_{10}-value defined as the change in rate for a 10°C change in temperature which operates from 0°C up to an optimum which is specified by the model user. The model user also specifies a maximum temperature, and the rate of loss declines linearly with temperature from the optimum to zero transformation at the maximum.

In summary these models use a first order reaction rate which is influenced by soil temperature and moisture. Only small differences in the way these influences are mathematically considered can be identified. Therefore it is to be expected that modelling results will stronger depend on a proper parameterization of these equations than on the choice of a specific model. Assistance for the choice of the parameters describing temperature dependency is given in chapter 1.

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Chapter 3

Validation of Models with Regard to Estimating Pesticide Concentrations in the Plough Layer

L. Bergström, A. Walker, J. Boesten, M. Businelli, M. Klein

Background

It is quite clear that verification and subsequent calibration are two of the most important constituents of the work involved in both model development and model testing, once a suitable experimental data set has been obtained. However, there is certainly no guarantee that the validity of the model extends beyond this data set against which the model has been calibrated. Validation, in the true sense of the word, is then the testing of the accuracy of the model against another independent data set; or, as earlier defined by FOCUS: ”comparison of model output with data independently derived from experiments or observations of the environment”. According to this strict definition, no input parameters should be obtained via calibration. In contrast, validation is indeed a thorough test of whether a previously calibrated parameter set is generally valid. Such rigorous model validation is, however, seldom performed. The reason for this is often the fact that model performance will almost inevitably be poorer than the results obtained during the calibration period. Simulation models are simplified representations of reality, which means that complex processes are commonly represented by model parameters that are considered as constants. However, this is not necessarily representative of reality, which means that we cannot expect calibrated parameter values to be generally valid. Even relatively well defined modelling scenarios dealing with pesticide dissipation in soils include parameters which often show considerable variation over time and with changing environmental conditions; *e.g.*: transformation rate constants (variations in microbial populations and/or activity), sorption/desorption coefficients (temperature dependence) and hydraulic properties (effects of soil management practices, swell/shrink, freeze/thaw). Also, many parameter values are determined in the laboratory under steady-state conditions, which are not representative of natural field situations.

The most common way of performing a validation test, although not quite in line with the above strict definition, is to use one data set divided into two separate parts. The first part is used to calibrate model parameters to match measurements. The second part of the data set is then used to validate the model, without additional calibration. The predictive capability of the model is thereby tested. This two-step validation scheme is recommended in the framework of COST Action 66 (Vanclooster *et al.*, 1995). However, when models are used as tools to support regulatory decisions, calibration as described here will usually not be possible since suitable experimental data is not available. Given such considerations, it is clear that parameter-estimation procedures which make use of default values and pedo-transfer functions (Petach *et al.*, 1991; Wagenet *et al.*, 1991; Hollis *et al.*, 1993), must be incorporated into most models if they are to be used in a regulatory context (Jarvis *et al.*, 1995*a*).

In general, validation of the models dealing with pesticide dissipation in soils has been more towards validation of the transport component of the models rather than predictions of pesticide concentrations in surface layers (Jones, pers. comm.). One exception to this is the simple model PERSIST (Walker & Barnes, 1981) which was developed primarily to simulate pesticide transformation in the surface soil layers, and which is now an integral component of some other, more detailed models (VARLEACH, PELMO). In the following presentation, the validation of the PERSIST model plus all of the models previously identified by the FOCUS group (GLEAMS, LEACHP, MACRO, PELMO, PESTLA, PLM, PRZM, VARLEACH) will be reviewed in the context of their use to predict pesticide concentrations in the plough layer. Some important factors for dissipation of pesticides in soil will also be reviewed.

Processes of Importance for the Occurrence of Pesticides in the Plough Layer

There are several conditions and processes that will determine the amounts of pesticides in the plough layer and their pattern of dissipation. Some of the more important ones are: volatilisation, interception by crop canopy and leaching. However, when dealing with modelling of pesticide dissipation in soil, such factors are often neglected or handled quite crudely. Also, model validation with regard to most of these processes (*e.g.* volatilisation) is rather limited. To some extent, this is due to the fact that we still have relatively poor quantitative knowledge about many of the processes, such as is the case for volatilisation. In other cases it is simply lack of proper measurements to be used as model input. For example, in a sensitivity analysis with the MACRO model, the fraction of the pesticide application which was assumed to be intercepted by the crop was shown to be one of the most sensitive parameters (Jarvis, 1991), although, this information was not readily available. The importance of accounting for the initial conditions, as correctly estimating the amounts of pesticide that reaches the soil surface, is stressed at several places below.

As indicated above, leaching is a process which potentially could have impact on field dissipation of mobile pesticides in the plough layer, due to its potential of moving the pesticide away from this layer. Preferential flow paths could increase this process by rapidly moving newly applied pesticide residues through the topsoil to the subsoil, without any interaction with the topsoil matrix. On the other hand, such bypass flow may also protect pesticide residues from leaching, if the compound is already mixed in with the soil matrix. Whichever condition dominates, it is a factor that potentially may contribute to poor resemblance between laboratory and field measurements of pesticide dissipation, and thus also between model predictions and measurements. However, it should be stressed that in the context of predicting pesticide dissipation in the plough layer, the reductions in concentrations due to preferential flow will likely be insignificant, as stated elsewhere in this document.

The influence of temperature on pesticide transformation is discussed elsewhere, as well as the present validation status with regard to temperature dependence.

Validation Status of the Models

PERSIST

The simple PERSIST model was developed to take account of the effects of varying soil temperature and moisture levels on rates of transformation in soil. It requires information concerning rates of transformation in a specific soil under defined laboratory conditions and then uses standard meteorological records (daily maximum and minimum air temperatures, rainfall, potential evaporation) plus a number of soil properties to make predictions of dissipation rates in the same soil in the field. The model has been tested in numerous situations in the field and, with compounds that are not volatile nor highly mobile, it can give accurate predictions of soil residue levels. In most situations, however, it overestimates soil residues presumably because only one dissipation process is included in the calculations. As mentioned above, the transformation routines from PERSIST have been incorporated into other more comprehensive models and these are discussed below.

VARLEACH

VARLEACH (Walker, 1987; Walker & Hollis, 1994) is a modified version of the CALF leaching model first described by Nicholls *et al.* (1982). Both models include the pesticide transformation routines described in PERSIST (Walker & Barnes, 1981). The CALF model was developed initially to simulate movement and persistence of residues in the plough layer and the results of several tests to compare predicted with observed soil residue data have been reported for both CALF (Nicholls *et al*., 1982; Walker, 1987) and VARLEACH (Walker & Welch, 1989; Moon & Walker, 1991; Businelli *et al.*, 1993; Trevisan *et al.*, 1995; Walker *et al.*, 1996). In most of these tests, detailed site-specific data were available and the models were tested without calibration. The results indicated that if all necessary input data were available for the specific soil/pesticide combination, good predictions of residue distribution in the soil could be obtained. When estimated rather than measured values for transformation rate or adsorption constant were used as input data, simulated results were often not good (Trevisan *et al.*, 1995), highlighting the site-specific nature of many of the input parameters. As discussed below with PRZM, VARLEACH also performs better overall with compounds that are not highly mobile in soil (Walker *et al.*, 1996).

The water-flow component of VARLEACH has been validated against limited lysimeter data, and predicted leachate volumes agreed well with those observed, and also agreed with data predicted by the more physically based LEACHM model. However, concentrations of pesticide in leachate were not well simulated, presumably because of the absence of preferential flow routines (Businelli *et al.*, 1993; Walker *et al.*, 1996). This indicates that models such as VARLEACH are more useful for predicting overall soil residues in the plough layer than for predicting either surface or groundwater contamination.

PRZM

Of the models included in this overview, PRZM is probably the most widely used and tested, at least in a context of regulatory decision support. However, in most of these cases, transformation rate coefficients were derived by calibrating the model against field measurements of residue concentrations in soil (Carsel *et al.*, 1986; Jones *et al.*, 1986; Lorber & Offutt, 1986; Sauer *et al.*, 1990), which disqualify them as validation tests. Still, some problems identified in these calibrated modelling tests are worth while mentioning: the lumping of different dissipation pathways into a single first-order transformation rate in the model (Carsel *et al.*, 1986); overestimation of downward water movement during summer, due to lack of upward fluxes of water and pesticide residues (Lorber & Offutt, 1986; Sauer *et al.*, 1990); and lack of kinetic sorption and preferential flow (Lorber & Offutt, 1986). However, these problems are certainly not only typical of PRZM, but also for several of the other models discussed here.

Even though most documented model tests with PRZM dealing with pesticide concentrations in surface layers have included calibration of the pesticide component of the model, some true validation tests have been performed. Loague *et al.* (1989*a,b*) compared PRZM model predictions of concentration profiles of the highly mobile, volatile compounds EDB, DBCP, and TCP to measured soil concentrations in structured fine-textured soils in Hawaii. The model failed to match the observed data, with concentrations generally over-predicted by several orders of magnitude. The authors attributed this poor model performance to a lack of model calibration. A similar conclusion was given by Loague & Green (1991), who tested PRZM against soil concentrations of atrazine measured at a field site in Georgia. They also mentioned the inability of the model to account for preferential flow processes as a contributing factor for poor model performance.

Better model performance was obtained in a test in which PRZM was compared with depth profiles of aldicarb and metolachlor (Parrish *et al.*, 1992).

Concentrations in soil of both compounds were satisfactorily described by the model, especially for metholachlor which remained in the upper 30 cm of the profile. It was concluded that the predictive capability of PRZM seems to be better overall when sorption is relatively high, such as is the case for metolachlor.

GLEAMS

GLEAMS is a model that to a great extent has been compared to measurements of pesticide residues in the plough layer. This reflects the original purpose for which the model was developed; *i.e.* elucidating transformation processes, pesticide efficacy, carry-over effects, and surface runoff/soil erosion. It is important to keep in mind that GLEAMS is not a predictive tool in the sense of absolute quantities (Leonard *et al.*, 1987). Consequently, predicted concentrations cannot be interpreted as absolute values, but rather be used to assess differences between management practices. Several tests specifically aimed at validating the model are reported in the literature (*e.g.* Leonard *et al.*, 1990; Sichani *et al.*, 1991). One such test was performed by Leonard *et al.* (1987), in which GLEAMS was compared with data representing a wide range of climate and soils. Compounds included in this comprehensive test were: alachlor, atrazine, and cyanazine. In general, model simulations represented the field data relatively well considering the great variability in the field data. Predictions suggested that neither alachlor nor cyanazine are expected to leach below the plough layer, which was in line with measurements. The predictions and observations of atrazine indicated leaching of atrazine to at least 30 to 40 cm depth.

Mueller *et al.* (1992) compared GLEAMS and PRZM simulations with soil concentration profiles of norflurazon, metribuzin, and alachlor in two loamy soils. Site-specific soil, environmental, and pesticide data were used without calibration. Both models slightly overestimated downward movement of the pesticides which resulted in underestimated concentrations in layers near the soil surface. Explanations given for this were: hysteresis in pesticide sorption and/or model errors in the calculations of soil water flow. Still, both models gave statistically adequate predictions of the total pesticide residues in soil.

In a model test performed in Finland, Salo *et al.* (1994) compared GLEAMS simulations with measured concentrations of trifluralin in a clay soil and a loamy sand. No model parameters were adjusted to fit the field data; only measurements and default values were used. The conclusion was that GLEAMS is able to predict trifluralin concentrations in the topsoil quite well, capturing the same decreasing trend and keeping the predicted concentrations within an order of magnitude of the measured ones. The authors attributed the constant pesticide transformation rate in GLEAMS as being the main reason for the discrepancy between field data and model output. It was also concluded that for pesticides with high adsorption coefficients, concentrations in the top few centimetres of soil are solely determined by transformation.

PELMO

The PELMO (Pesticide Leaching Model) model was tested against 19 lysimeter studies (39 individual lysimeters including variations or parallel lysimeters) performed in Germany at different locations between 1987 and 1991. Fourteen different pesticides were included in this project. Even though this study was mainly focused on pesticide leaching, simulated and measured concentrations in the soil were also compared.

Comparison of the measured and simulated hydrology results showed that PELMO did in principle reflect the seasonal water movements in the lysimeters quite well. PELMO 2.0, which considers crop specific Haude factors when estimating evapotranspiration, was able to predict both low-intensity and high-intensity leaching scenarios in agreement with experimental results. The average deviation between measured and simulated amounts of leachate was twice as high as the deviation observed for parallel lysimeters. Comparing measured and simulated pesticide concentrations in the different soil layers showed a slight tendency of the model to overestimate pesticide transformation. This was presumably due to the limited data available on temperature and moisture effects on transformation. Also, the deviation between measured and predicted pesticides concentrations in soil were within one order of magnitude for more than 71 % of the studies. It should also be noted that all simulated results were obtained without calibration, both with regard to hydrology parameters as well as pesticide parameters. Publication of this study is in preparation.

LEACHP

In a validation test with LEACHP, Wagenet & Hutson (1986) demonstrated good agreement between field measurements and predictions of aldicarb residues in a sandy loam soil. The compound was largely confined to the plough layer (down to 30 cm), with only trace amounts detected to 60 cm. The best agreement was obtained when the variability in measurements was considered. This infers that the transformation process was both spatially and temporally variable in the field, making it necessary to vary the transformation rate coefficients (k_r) in the simulations, both with time and space. Consequently, it may be inappropriate to use laboratory-derived values on k_r, since they do not always represent the variation in transformation rates to be expected in the field. However, the authors concluded that such laboratory derived values can still provide a reasonable first estimate of the rate of transformation.

In another more recent model test, the predictive ability of LEACHP (together with VARLEACH and PRZM2) was evaluated for a number of data sets originating in the UK, Germany, France and Italy (Walker *et al.*, 1995). The pesticides included in this test were: alachlor, metribuzin, metsulfuron methyl, terbuthylazine, metamitron and chloridazon. For the first three compounds, which were tested in the UK, LEACHP (as well as the other two models) generally gave acceptable predictions of the distribution of residues in the plough layer. As mentioned elsewhere in this overview, this was particularly the case for the less mobile compounds, such as, alachlor. For the terbuthylazine data set obtained in Germany, LEACHP gave satisfactory results in 36 % of the comparisons, if the proposed model efficiency criteria were considered. Of all simulations of transformation with both the German and French data sets, and all models, only 23 % were considered accurate (*i.e.* within 20 % of the measured values), with LEACHP showing a slightly better performance than VARLEACH and PRZM2. The predictive ability of LEACHP when tested against the Italian data sets (metamitron and chloridazon) was difficult to evaluate, due to the large variability in model performance depending on which data set was used. The same was true for the other two models.

MACRO

The predictive capability of the dual-porosity model MACRO was tested against a data set including alachlor concentrations in the upper part of a sandy loam soil profile (down to 40 cm), without calibration (Jarvis *et al.*, 1995*b*). The model predictions were based on parameter estimates derived from a combination of default values supplied with the model, mean soil properties obtained from the SEISMIC database system (Hollis *et al.*, 1993), pedo-transfer functions, and compound properties (K_{oc} and $t_{1/2}$) obtained from experiments carried out at other locations. The model performed quite well, considering the fact that site-specific data was not used. Residue concentrations in the upper 10 cm of the soil profile were closely matching measurements, and predicted and measured concentrations in suction probes at 25 and 40 cm depths were mostly within a factor of two.

In another model test, MACRO simulations were compared with measurements of metamitron, methabenzthiazuron, and simazine concentrations in the 0-10 cm layer of a German loamy soil (Jarvis, 1995). No calibration of the pesticide part of the model was performed, only some adjustment of parameters related to root water uptake. Transformation rates typical of laboratory conditions were used in all simulations. After having matched the initial amounts of herbicide in the soil, the model performed satisfactory, with herbicide concentrations mostly lying within the 95 % confidence limits of the measurements.

PESTLA

The PESTLA model was tested against field data (0.4 ha plot) on persistence of autumn-applied ethoprophos in the top 20 cm of a sandy soil (Van den Bosch & Boesten, 1994). No calibration of the pesticide part of the model was performed and input on transformation rates was based on site-specific laboratory studies at three temperatures. After having matched the initial pesticide amount in the soil (which was half of the amount sprayed, probably due to volatilisation during the first few days after application), the model explained the decline observed during the first ca. 200 days in the field very well. Thereafter, the decline in the field was faster than measured in the laboratory, possibly due to the presence of a full-grown crop (winter wheat).

In another study, the PESTLA model was tested against field data on persistence of spring-applied bentazone in the top 30 cm of a sandy soil (Boekhold *et al.,* 1993). Input was based on a site-specific laboratory study at one temperature. After having matched the initial amount in the soil, the model performed well during the first two months; *i.e.* calculated concentrations were within one standard deviation of the measured ones. One additional test describing the conditions 11 months after application, resulted in calculated values being less than 0.001 mg/kg compared with measured soil concentrations in the order of 0.01 mg/kg.

PLM

PLM is one of two models in this overview which takes preferential flow behaviour into account. In contrast to MACRO, which is the other preferential flow model, the water/solute flow components in PLM are not physically based which reduces the requirement for ”difficult-to obtain” soil physical parameters. This ought to make the model user friendly, but will also inevitably increase the need for calibration. Since PLM was developed relatively recently, it has not yet been validated in terms of accuracy in predicting pesticide concentrations in the plough layer.

Conclusions

The validation status of PERSIST is reasonable for compounds that are not volatile or highly mobile. The validation status of other models in this overview is rather poor with regard to pesticide dissipation in the plough layer. This is to a large extent a reflection of the main purpose for which the models were developed, *i.e.* to predict surface runoff and leaching in the unsaturated zone. Therefore, further testing and validation against persistence data is needed to improve our confidence in the capability of the models to predict pesticide concentrations in the plough layer. Still, there are several dissipation pathways which are not included or crudely dealt with in the models considered here, which will ultimately impact on their validity. In general, the models are weak in terms of coping with loss processes at the soil surface (*e.g.* volatilisation and photo-decomposition). Also, a critical factor such as interception of pesticide on the crop canopy, which has a large impact on the mass balance in soil, requires much more attention. The inconsistency between parameter values determined in the laboratory and under field conditions (*e.g.* transformation rate coefficients) is yet another problem which needs thorough consideration in the future. Taking these considerations into account, there is reason to believe simulation models will continue to be used in the future in the regulatory process to address various issues related to registration of pesticides.

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Summary of the validation tests included in this overview

Model	Pesticides	Type of measurements	Soil types	Ref.[a]
VARLEACH	Chlorsulfuron, metsulfuron methyl, triasufuron	Coring, 50 cm	Sandy loam	31
	Alachlor,	Columns, 30 cm	Sandy loam	16
	Alachlor, metolachlor, linuron	Lysimeters, 150 cm	Sand, silty clay, sandy/silty clay loam,	2
	Metamitron	Coring, 30 and 50 cm	Silt loam, clay loam	24[b]
	Alachlor, atrazine, metribuzine	Columns, 30 cm	Sandy loam	34[c]
PRZM	EDB	Drilling, 2000cm	‘Fine-textured’	13
	EDB, DBCP, TCP	Drilling, 2000 cm	‘Fine-textured’	14
	Atrazine	Coring, 26 cm	Sandy clay loam, sandy loam, loam	14
	Aldicarb, metolachlor	Coring, 120 cm	Sa loam/Sa clay loam	19
GLEAMS	Cyanazine, alachlor, atrazine	Coring, 10 and 40 cm	Silt loam, sand, sandy loam	10
	Norflurazon, metribuzin, alachlor	Coring, 60 cm	Sandy loam/sandy clay, Loamy sand/sandy clay loam	17
	Trifluralin	Coring, 25 cm	Clay, loamy sand	21
PELMO	‘14 pesticides’	Lysimeters, 100 cm		unpubl.
LEACHP	Aldicarb	Coring, 150 cm	Sandy loam	27
	Alachlor, metribuzin, metsulfuron methyl, terbutylazine, metamitron, chloridazon	Lysimeters, field dissipation studies		33
MACRO	Alachlor	Suction cups/coring, 150 cm	Sandy loam/loamy sand	8
	Methabenzthiazuron, metamitron, simazin	Coring, 10 cm	Silt loam	6
PESTLA	Ethoprophos	Coring, 20 cm	Sand	26
	Bentazone	Coring, 30 cm	Sand	1

[a] The numbers refer to the reference list.

[b] Reference 24 compared VARLEACH, PRZM-2, PESTLA and LEACHP with the same data sets.

[c] Reference 34 compared VARLEACH, PRZM and LEACHP with the same data sets.

Chapter 4

European scenarios for behaviour of plant protection products in soil

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1 Introduction

Fixed scenarios are used in some countries of the European Union to estimate the possible behaviour of plant protection products in the environment and to evaluate the registerability of the product in the country. For instance, the leaching potential of plant protection products to groundwater is estimated in this way in Germany and the Netherlands (Klein and Knoche, 1995). It is generally agreed that the use of standard scenarios in estimating Predicted Environmental Concentrations (PEC's) might be useful in the process of evaluating the possibilities for registration of a plant protection product and therefore, the FOCUS Leaching Modelling Group proposed 10 scenarios for predicting the leaching behaviour of plant protection products in Europe (Document 1694/VI/95 and Document 4952/VI/95). However, they recognised that at the time of establishing the scenarios, information was not readily available and that some changes in the scenarios might be necessary in the (near) future. In this chapter scenarios for estimating PEC's in soil will be elaborated. The results, however, also apply to leaching and, therefore, can be used to change the leaching scenarios as developed by Klein and Knoche. Section 2 gives basic ideas for the construction of scenarios and section 3 gives the scenarios themselves. In section 4 the scenarios are discussed and finally in section 5 conclusions and recommendations are given.

2 Scenario construction

Klein and Knoche (1995) give four categories of data and parameters which are necessary input for the calculation of a PEC:

- plant protection product parameters
- soil data and soil parameters
- climate data
- crop data and crop parameters

Of course the categories are not entirely independent (for instance, soil development is dependent on the climatic conditions and some soils are more suitable to a specific crop than others), but for the construction of scenarios the categories are considered independent.

A scenario is here defined as a full set of data and parameters necessary for the calculation of a PEC, excluding the plant protection product parameters (DOC 4952/VI/95). In the context of the authorisation evaluation, a plant protection product is the subject of the evaluation, and therefore plant protection product parameters are not regarded as part of a scenario.

A scenario should contain all necessary input data for (any) calculation method (including dynamic simulation models) that might be chosen. (For the time being, any calculation method that is approved by national or international authorities responsible for the evaluation of plant protection products). In general this means that input data have to be available for the four categories mentioned above; for dynamic simulation models the data have to be available as a function of time. PEC's can be calculated by running a model using a scenario and plant protection products parameters as input.

A number of sensitivity analyses has been performed regarding the influence of scenario data on the leaching of plant protection products to groundwater using the simulation models PESTLA and PESTRAS (Boesten, 1991; Swartjes, 1993; Tiktak, 1993). Although some conclusions are specific to the leaching process, the results are useful when considering the behaviour of plant protection products in the soil environment in general. The papers of Boesten, Swartjes and Tiktak agree in the conclusion that the sensitivity of the model to model inputs is strongly dependent on boundary and initial conditions. In general they conclude that leaching is:

- highly sensitive to pesticide properties (sorption and transformation)
- moderately sensitive to climatic conditions
- almost insensitive to soil properties (as far as the standard Dutch scenario is considered and the soil properties do not directly interfere with sorption).

The third conclusion is not applicable to compounds that show hardly any sorption (Tiktak, pers. communication). Of course these observations are based on the assumptions made in the simulation models. As a first approach these sensitivities also apply to the behaviour of plant protection products in the soil environment.

Combining the categories given above with the sensitivities, the following data and parameters are important in the construction of a scenario:

- soil organic matter (and for some compounds clay content and CEC) as they influence the sorption of a plant protection product in the soil

- climate data; temperature because of its influence on the transformation rate and precipitation because of its influence on the transformation rate and the leaching of the plant protection products out of the root zone
- soil texture
- crop data as plants influence the behaviour of moisture in the soil (and therefore have influence on the transformation and the leaching) and as they may take up plant protection products from the soil. This is especially important if sorption is low and/or transformation is low. The latter parameter may therefore be influenced by the temperature differences between the scenarios.

As already stated above, the different parameters and data interact and therefore there is not a unique approach to the construction of a scenario. One may choose different starting points for the scenario construction, e.g. starting with the soil, the climate or the crop. The choice of the starting point very much depends on the goal of the scenario. If, for instance, one wants to predict the behaviour of a specific plant protection product and this plant protection product is especially meant for a specific crop, the starting point can be the crop. Given the crop, one then selects the soils on which the crop may grow and completes the scenario by defining the climatic zones. (This approach has been suggested by Delmas and Guyot). If on the other hand one wants to construct scenarios that can be used as a first approximation for a broad range of pesticides, one may start with the climate and then add the soil and crop to it. This latter approach was followed by Klein and Knoche (1995, DOC 4952/VI/95) and is also used in the remainder of this text. The reason for this approach is the intended use of the scenarios: a first approximation to the calculation of PEC’s for a broad range of pesticides used within Europe. (These scenarios are meant to be used in the first step or the first few steps of the evaluation of a plant protection products.)

The different approaches will deliver results that come closer to each other when the scale of a scenario becomes larger (when the area of a scenario becomes smaller). Ultimately the results will become the same when the variability in soils, climate and others parameters becomes negligible.

3 Soil - climate scenarios

Based on the boundary conditions described in section 2 soil - climate scenarios were derived as follows:

1. Using data on long-term average annual sums of precipitation and evapotranspiration, a map was constructed in which areas were defined according to classes of the net precipitation amount.
2. Using data on the average annual temperature a map was constructed in which areas were defined according to classes of this average temparature.

3. An overlay of 1 and 2 was made and combined classes of net precipitation / average temperature were defined. The number of classes should not be too large.Choosing boundaries as given in table 2, the number of climate classes turned out to be 8. This was considered convenient.
4. Subsequently, the combination map was smoothed by selecting the predominant class in an area (*In the ARC/INFO software language the ZONALMAJORITY command was used to perform the smoothing).* In this manner, figure 1 has been obtained. The areas constructed in steps 1 through 4 are now referred to as climate areas. In tables 1 through 5, the scenario regions are described in some detail. For each area more or less representative weather stations were chosen for which characteristic data on temperature are recorded. These data are given in table 9. For scenarios 1 and 2, no monthly data were available. Also, the annual data are available per grid cell only (no weather station information is available).
5. Using the soil map, the landuse map (see for meta-information on these databases section 6) and the climate area map the relative abundance of soil types was calculated for each defined climate area. In table 3, the soil types are listed in descending order of abundance (the relative abundance is given as the percentage of area within which landuse ‘arable land’ is dominant). Within an area other soils might be more abundant, but they are not in agricultural use. In table 4, the relative abundance of arable land (relative to total area of a climate area) is given. Tables 5 to 7 state characteristics of the soils. Since the FAO soil classification is based on genetic features (parent material, formation processes) and not on physical/chemical characteristics (hydraulic conductivity, texture), the soil type and the soil characteristics definitions within each scenario region were determined independently.
6. As under 5, using data from EUROSTAT, for each climate area the ranking of crops was determined. Table 8 lists the crops for the different areas in descending order of abundance. Data on crops for scenarios 1 and 2 were also not available.

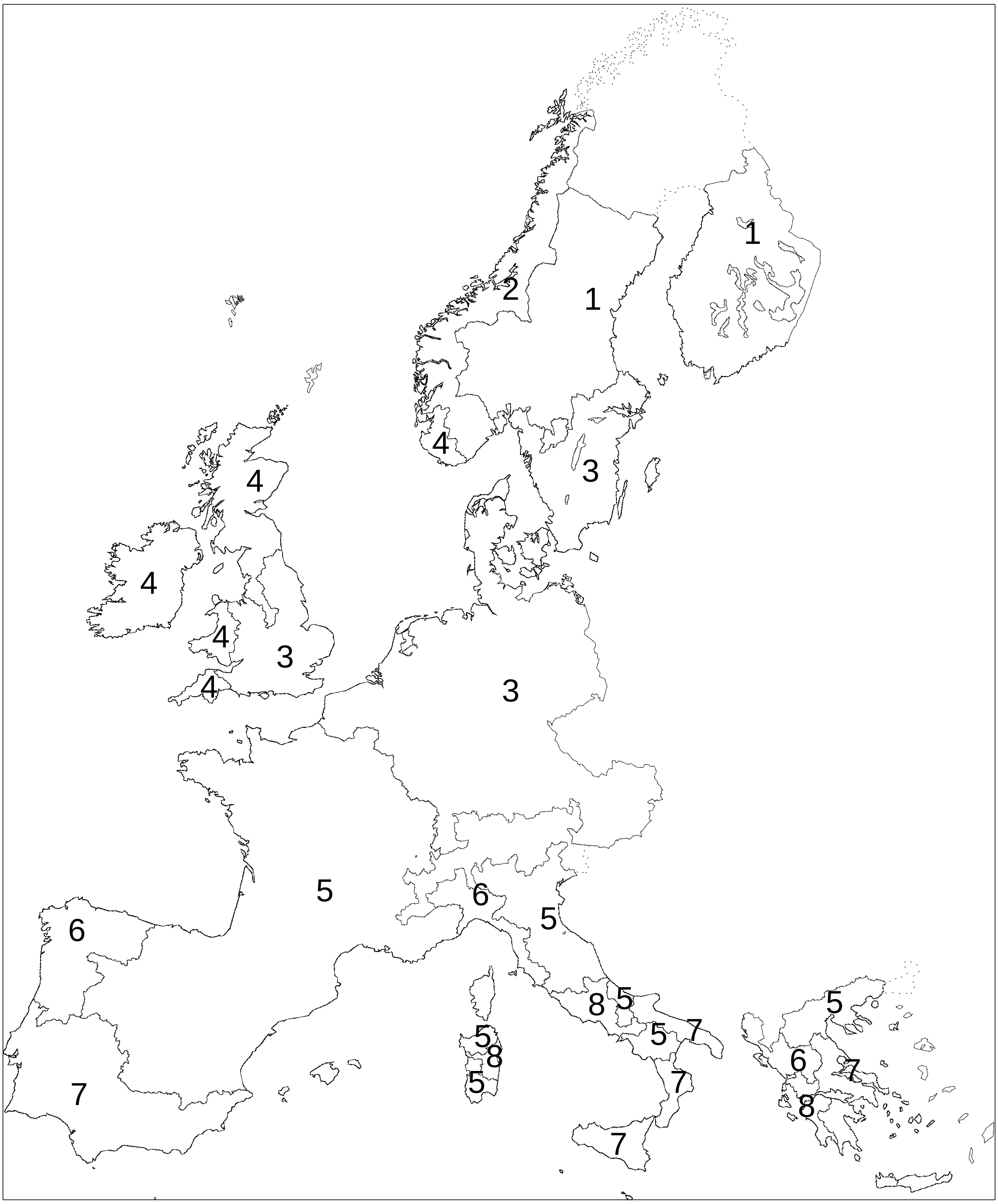

Figure 1.: Scenario regions in Europe, based on combination of net precipitation and temperature.

TABLE 1.: Topographical description of the scenario regions.

Scenario number	Description
1	Central Sweden, Finland
2	Norway
3	South Sweden, South-East England, Denmark, Belgium, Netherlands, Luxembourg, Germany, Elzas (France)
4	Ireland, Scotland, North England, West England, Wales
5	France, North-East Spain, North-Central Italy, Sardinia, West Corsica, North East Greece
6	North-West Italy, North-West Greece, North Portugal, North-West Spain
7	South-Spain, South Portugal, South-Italy, Sicily, South-East Greece
8	East Corsica, Central Italy, West Greece

TABLE 2.: Definition of the climatic scenarios

Scenario number	precipitation excess class (mm yearly)	temperature class (°C annual average)
1	<400	0-5
2	>400	0-5
3	<400	5-10
4	>400	5-10
5	<400	10-15
6	>400	10-15
7	<400	15-20
8	>400	15-20

TABLE 4.: Areal percentage of climatic area within which arable land is the dominant land use.

Scenario number	areal percentage arable land
1	4.2
2	0.1
3	51.4
4	6.2
5	52.2
6	36.4
7	45.9
8	31.9

TABLE 3.: Relative abundance of the dominant soil types (FAO classification) within dominant arable land areas in each scenario region

Scenario number	ranking	dominant soil types	relative abundance (%)
1	1	orthic podzols	63.4
	2	vertic cambisols	18.9
	3	undefined by FAO	3. 9
	4	lithosols	3. 6
	5	dystric gleysols	2.7
2	1	orthic podzols	45.5
	2	undefined by FAO	45.5
3	1	orthic luvisols	24.7
	2	dystric cambisols	11.7
	3	eutric cambisols	10.0
	4	humic podzols	8.6
	5	orthic podzols	5.6
4	1	dystric cambisols	36.2
	2	eutric gleysols	16.9
	3	orthic luvisols	11.7
	4	humic gleysols	10.0
	5	placic podzols	6.9
5	1	calcic cambisols	18.5
	2	eutric cambisols	18.4
	3	orthic luvisols	15.3
	4	dystric cambisols	11.4
	5	gleyic luvisols	10.0
6	1	humic cambisols	32.5
	2	eutric cambisols	13.2
	3	lithosols	9.2
	4	rankers	8.9
	5	gleyic cambisols	6.9
7	1	eutric cambisols	25.6
	2	calcic cambisols	19.9
	3	eutric regosols	10.3
	4	lithosols	8.0
	5	chromic luvisols	6.2
8	1	eutric cambisols	42.3
	2	mollic andosols	24.7
	3	dystric cambisols	13.1
	4	chromic luvisols	9.6
	5	eutric regosols	2.9

TABLE 5.: Relative abundance of texture classes and organic matter within dominant arable land areas in each scenario region.

Scenario number	ranking	texture class[$]	organic matter (%)[#]	relative abundance (%)
1	1	2	3-4	44.4
	2	7	2-3	16.6
	3	1	3-4	16.3
	4	2	2-3	4.6
	5	2	<1	3.0
2	1	4	3-4	45.5
	2	1	<1	45.5
3	1	4	1-2	23.9
	2	4	2-3	16.3
	3	1	3-4	11.8
	4	6	4-5	6.1
	5	6	2-3	4.3
4	1	2	2-3	22.0
	2	4	1-2	14.0
	3	4	8-10	12.7
	4	4	3-4	9.8
	5	4	2-3	7.1
5	1	6	2-3	30.2
	2	4	2-3	22.6
	3	4	1-2	15.0
	4	6	4-5	6.4
	5	2	2-3	5.2
6	1	4	4-5	29.9
	2	4	2-3	22.1
	3	6	2-3	9.4
	4	6	<1	9.0
	5	6	3-4	5.1
7	1	6	2-3	25.0
	2	4	2-3	19.9
	3	6	<1	13.2
	4	6	1-2	7.8
	5	4	<1	5.3
8	1	6	2-3	33.5
	2	4	10-14	24.3
	3	4	2-3	17.5
	4	6	1-2	6.3
	5	6	<1	4.5

$: See Table 6 for Description of the soil texture classes.

#: The organic matter data are based on estimates (Fraters and Bouwman, 1993).

In the soil texture map of Europe, the texture class numbers can be explained as follows:

TABLE 6.: Description of each texture class according to FAO.

Soil map class number	**Description**[@]
1	1
2	1/2
3	1/3
4	2
5	1/2/3
6	2/3
7	3
8	Histosols
9	Dunes
10	Rock Debris
11	Glacier
12	Salt Flats
13	Non Europe
14	Water

[@] The numbers in Table 6 denote the texture classes as defined by FAO (Soil map of the world):

1.: Coarse, i.e. sands, loamy sands and sandy loams;

2.: Medium, i.e. sandy loams, loams, sandy clay loams, silt, silty clay loams, and clay loams,

3.: Fine, i.e. clay, silty clays, sandy clays and clay loams.

Table 7 gives their particle size distribution.

TABLE 7.: FAO texture class description.

Texture class	%clay	%silt	%sand
1	<18	<17	>65
2	<35	>0	<65
3	>35	-	-

TABLE 8.: Dominant crops in the scenario regions.

Ranking	**Scenario**[#]					
	3	4	5	6	7	8
1	wheat	barley	barley	maize	wheat	wheat
2	barley	wheat	wheat	wheat	barley	barley
3	sugar	potato	maize	rye	rye	potato
4	potato	sugar	rye	potato	sugar	rye
5	maize	rye	potato	barley	maize	miaze

[#] Information for scenarios 1 and 2 is missing in the database.

TABLE 9.: Monthly and annual average (long year average) air temperatures (ºC) for representative weather stations in scenario regions 3 - 8 (Source: CORINE).

station name	**station no**	**country**	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**annual**
Scenario 3															
Uppsala		S	-0.90	-1.30	-0.60	2.30	9.10	13.90	15.90	14.70	10.50	6.00	2.20	0.00	6.00
Stroemmen	90008	DK	-0,50	-0,60	1,70	6,40	11,10	14,70	16,90	16,30	13,00	8,50	4,60	2,20	7,90
Luedingshausen	10398	D	1,50	1,80	5,00	8,90	13,00	16,10	17,60	17,20	14,30	9,80	5,80	2,80	9,50
Aulendorf	10764	D	-2,50	-1,10	3,00	7,20	11,60	14,90	16,70	16,10	13,00	7,60	2,60	-1,10	7,30
De Bilt	40006	NL	1,70	2,00	5,00	8,50	12,40	15,50	17,00	16,80	14,30	10,00	5,90	3,90	9,40
Pershore	70188	GB	3,60	3,90	6,00	8,90	11,80	15,00	16,70	16,30	14,20	10,90	6,80	4,70	9,90
Scenario 4															
Casement airdrome	80211	IRL	4,40	4,40	6,00	7,80	10,50	13,30	14,90	14,60	13,00	10,30	6,70	5,30	9,30
Scenario 5															
Aerodrome D'aulnat	20274	F	2,80	3,80	7,50	10,20	13,60	17,20	19,20	18,90	16,40	11,40	6,90	3,60	11,00
Caceras	110164	E	5,20	5,80	7,30	10,60	14,40	18,30	21,80	21,50	18,00	13,40	8,10	5,30	12,50
Bologna	30002	I	2,10	4,30	9,10	14,10	18,30	23,00	25,70	25,00	21,20	14,80	8,70	3,90	14,20
Scenario 6															
Dunas de Mira	120339	P	9,80	10,60	12,90	14,40	15,90	18,00	19,00	19,10	18,50	16,20	13,20	10,40	14,80
Massa	30046	I	6,80	7,50	10,30	13,30	16,90	21,20	23,70	23,30	20,60	16,00	11,30	7,90	14,90
Ioannina	100019	GR	5,20	6,30	9,00	13,00	17,50	22,20	25,50	25,00	20,60	15,30	10,40	6,70	14,70
Scenario 7															
Aracena	110135	E	12,00	13,90	17,70	17,90	20,40	24,70	30,00	30,00	25,70	18,70	14,80	12,10	19,80
San Giuseppe Jato	30186	I	8,00	8,50	11,10	14,60	18,50	23,40	26,30	26,30	23,20	18,20	13,60	9,70	16,80
Nauplion	100039	GR	10,30	11,00	12,40	16,20	20,60	25,30	28,50	28,00	24,20	19,70	15,80	12,00	18,70
Scenario 8															
Roma	30077	I	6,90	7,70	10,80	13,90	18,10	22,10	24,70	24,50	21,10	16,40	11,70	8,50	15,50

4. Discussion

Particularly in the Nordic countries, there is a great interest in having realistic worst case scenarios for calculating PEC’s (in soil and groundwater). One of the reasons for this is that there is a widespread use of plant protection products in early spring and in late summer or autumn. In these periods the temperatures may be rather low and this may influence the persistence of the compounds in the soil and the leaching to the groundwater. A longer persistence may cause carry over problems in following crops, but also make a plant protection product more liable to leaching. Besides an adequate description of the relation between soil temperature and the transformation rate of a compound in the soil (compare chapter 1) adequate scenarios for these regions are required. The relation between temperature and the transformation rate might be a Q10 relationship, but, especially for the colder periods, an actual correlation might be preferred. Because of a lack of data in available data sources, the scenarios 1 and 2 could not be worked out in detail in tables 8 and 9. An indication of the importance of the low temperatures can be obtained from table 9 for the weather station Uppsala. The city of Uppsala is within the area covered by scenario 3, but the location is not very far from the area covered by scenario 1. The area used for arable farming under scenarios 1 and 2 is not very large, but the situation is very different from other scenarios and, therefore, these scenarios deserve more attention.

The scenarios described in section 3 were derived from maps and data that are not very accurate. In general the data used is available at low or no costs. For instance, for the soil descriptions the soil characteristics were derived from ranges given to the soil classes and general profile descriptions. Better data are available (for instance at ISPRA), but these data were inaccessible within the limits of the FOCUS group.

The scenarios represent long term average conditions for each region. In order to obtain scenarios for realistic worst case conditions, data have to be analysed further.

The data on temperature, as given in table 9, were not analysed for their representativiness for the area. The table is included for easy reference and, therefore, for some areas more than one station is included.

With regard to the soil characteristics, it can be stated, that the FAO classification is based upon genetic features and not on physical characteristics as is the STIBOKA (Winand Staring Series) classification. The data on texture are therefore rather limited. This means, that worst case scenarios will be represented by rather coarse data with regard to soil. Better data were not available within the remit of the project.

5 Conclusion and recommendation

Soil - climate scenarios were constructed which can be used in the first step (or first few steps) of the registration evaluation of plant protection products in Europe. The scenarios given represent average environmental conditions for the areas. A first estimate of predicted environmental concentrations of a plant protection product in soil (and groundwater) can be obtained by using the defined scenarios. To obtain also PEC's for realistic worst case conditions, data have to be analysed further. In further steps of the evaluation more refined scenarios should be used in order not to overestimate or underestimate the concentrations that might occur in reality. In principle, the data currently available are sufficient to generate input for PELMO and PESTLA/PESTRAS.

Tiktak et al (1995) propose a refined approach (for the Netherlands), which also concerns GIS methods. In this method, no scenario regions are defined, but all input maps (precipitation, evapotranspiration, temperature, soils, organic matter classes, and landuse) are combined in GRID-format. The resulting grid consists of all combinations of the maps above; scenarios are formed by each unique combination in the GRID.

For Europe, this might imply a very laborious operation, especially considering the data currently available. Furthermore, this is in contradiction with the requirement, that the number of scenarios cannot be too large. One alternative may be to narrow the precipitation and temperature classes, which, however, may still lead to more scenario regions. Another alternative might (taking the current data as a basis) be to calculate for each of the 5 dominant combinations within a scenario region and to calculate a weighted average PEC or a (weighted) PEC range for each area with an uncertainty distribution.

The scenarios were constructed using rather uncertain data on soil types and their characteristics. The scenarios might be substantially improved if more accurate data become avaible; if possible at a high level of detail. The data we are looking for must be based on measurements and not on estimates as was often the case for the scenarios constructed in section 3.

It is recommended that a research is started in which the scenarios are analysed for their representativity for the chosen areas. Not until such a study has been completed, one can characterise the soil-climate scenarios with respect to their accuracy in estimating PEC's.

6. Meta-information on databases used

Database: EUGRID6_PAN
Description: Pseudogrid of 1/6x1/6 degree. This database is the spatial database to which soil and meteo data are related to obtain the scenario map and the ranking of soil types.
Owner (source): RIVM (EUROSTAT)

Database: SOIL_PAN
Description: This database contains dat on soil types and characteristics (texture, organic matter, slope, etc) for Europe, based on the FAO classification. It is related to EUGRID6_PAN.
Owner (source): UNESCO/FAO/RIVM

Database: METEO_PAN
Description: This database contains net precipitation (annual total; long year average) and temperature (annual average; long year average) for Europe. It is related to EUGRID6_PAN.
Owner (source): RIVM (EUROSTAT)

Database: EUROPE_PAN
Description: Administrative regions (NUTS3-level) in Europe. This map is used as a reference to perform the ZONALMAJORITY command in ARC/INFO grid.
Owner (source): EUROSTAT

Database: LU_EUROGRID
Description: This is essentially the same database as EUGRID6_PAN. It is however, used to relate landuse data for Europe.
Owner (source): RIVM (EUROSTAT)

Database: LUGRID_TABLE
Description: This file contains landuse data for Europe. It is used to obtain ‘arable land’ and to determine the relative abundance of soils within arable land. It is related to LU_EUROGRID.
Owner (source): RIVM

Database: CLIM_STAT_EC
Description: Meteo stations (represented as points) in the EC (not entire Europe). It is used to relate to temperature data on monthly and annual basis in order to obtain table 9.
Owner (source): CORINE

Database: CLIMATE_EC_MMAT

Description: This file contains the temperature data on monthly and annual basis (averages, long year) for each weather station. It is related to CLIM_STAT_EC.
Owner (source): CORINE

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Chapter 5

Recommendations for the Calculation of Predicted Environmental Concentrations in Soil

R. Jones, R. Kloskowski, and V. Vanderbroeck

Estimates of the concentrations in the surface layer of soil can be useful in assessing the environmental impacts of crop protection chemicals. Such assessments include potential ecotoxicological effects such as acute and long term effects on earthworms and or soil organisms, impact on soil concentrations at the time of harvest or planting of following crops, accumulation and build-up of residues in soil, and the effect of multiple applications.

A variety of approaches can be used for estimating concentrations of crop protection chemicals in the surface layer of soil. These range from simple models to complex simulation models often used to describe transformation and movement in soils. A phased approach is recommended with the simple models often being sufficient, but more complex simulation modelling is helpful under some circumstances. These phased approaches are outlined in the flow diagrams (Figures 1-3). Normally, assessments would begin with the simplest approaches and move to the more comprehensive as needed, but a more comprehensive approach can always be substituted for a simpler approach.

The simplest models are based on the application rate and a specified mixing depth, soil bulk density, and percent of applied material reaching the soil. Examples of such models include the procedures described in the EU registration guidelines and EPPO and BBA guidelines for earthworms. These parameters permit the calculation of the concentration in the surface layer of soil immediately after application. Often such calculations are sufficient to indicate that concentrations will be below levels resulting in ecotoxicological impacts. Predicted soil concentrations using these simple models may vary significantly depending on the input values (such as mixing depth) specified by the assessment procedure.

The results of these simple models are directly proportional to the value chosen for the amount of material reaching the soil surface. Variables affecting this value for foliar applications include the crop, the growth stage, the details associated with the application procedure, and agricultural practices such as row spacing and number of seeds per meter of row. Wash off from the foliage to the soil surface may also affect soil concentrations and variables affecting wash off include the sorption and transformation of the crop protection chemical on foliage, the amount and intensity of rainfall, and the timing of rainfall relative to the application date. The guidance in the EU registration dossier of using a value of

50 percent for applications to foliage, but allowing the use of specific data (when available) seems appropriate.

If necessary, time-weighted average concentrations can be calculated which consider the decreases in surface layer concentrations with time (for example, using the TWA model). With the additional conservative assumptions of no losses due to runoff, leaching, or volatilisation, an upper limit on the residue concentrations in the surface layer of soil can be determined as a function of time (as in the TWA, EFATE, and the Dutch build-up models). Usually first order kinetics are used to describe the concentration as a function of time (especially for the time-weighted concentrations), but such calculations can also be performed for other kinetic expressions. When using kinetic expressions other than first order, care must be taken that the concentrations in the layers are similar to those in which the kinetics were derived. For example, transformation kinetics for a second order reaction would be calculated to be much faster following an application to the soil surface where residues are present in the upper few millimetres of soil than in a laboratory study where residues are distributed uniformly throughout the soil.

More complex approaches are usually focused on quantifying the impact of runoff, leaching, and volatilisation on concentrations in the surface layer of soil, resulting in lower concentrations than using the simpler calculations. In such cases an appropriate simulation model would normally be used to simulate these processes. Examples of such models have been described in the output from the FOCUS Leaching Workgroup. Modelling of surface soil concentrations is more accurate than predicting concentrations in or movement through subsoils. In general shapes of predicted concentrations often do not precisely match measured soil concentration profiles, but they do a relatively good job of predicting the main portion of the residue plume. As shown in Figure 4 there are typically three differences between measured and predicted concentration profiles. Usually a small portion of the residue plume moves more rapidly downward due to preferential flow processes. However under most conditions, the most important process for downward movement of residues out of the surface layer of soil will be classical leaching and reductions in surface concentrations due to preferential flow will be insignificant. Often movement of the main portion of the residue plume is slower than would be predicted. However, the effect of slower movement on concentrations in the surface layer of soil is usually more than offset by faster transformation under field conditions than would be expected from laboratory experiments. Therefore, simulation models, like the simple models, often overestimate concentrations in the surface layer of soil.

Simple models are usually of sufficient accuracy when assessing effects soon after application (such as potential acute effects on earthworms). Simulation models may be needed for assessments over longer time periods (such as residues in surface soils at the time of harvest or planting of subsequent crops), especially for volatile or mobile compounds. Since the simple models provide an upper bound to soil residues, use of simulation models should not be necessary when concentrations estimated by the simple models are not high enough to indicate potential concerns.

In some circumstances, estimates of concentrations in the surface layer of soil must consider multiple applications. A first step would be to calculate the concentration following a single application consisting of the total amount applied in the multiple applications. If necessary, the concentration after the last application can be easily refined with the additional assumption that residues from multiple applications are additive. Then the contribution of each application to the concentration immediately after the last application can be determined using the appropriate kinetic expression for transformation. Using the calculated soil concentration after the last application, the time-weighted average values can be calculated using the same procedure as for a single application. As mentioned earlier for single applications, if necessary more precise values of surface soil concentrations can be calculated using simulation models. Most of the simulation models allow for multiple applications, so the additional complexity associated with multiple versus single application simulations is minimal.

One use of the simple model approach with multiple applications is the prediction of the build-up of residues in the surface layer of soil as a result of annual applications of persistent pesticides (for example, using the first order residue build-up model). Such an analysis indicates that residue levels following repeated yearly applications of an immobile compound with a half-life of six months will plateau at about 1.33 times the levels following the first application. For half-lives of 9, 12, and 24 months, maximum residue levels will 1.66, 2.00 and 3.41 times the levels following the first application. The build-up of more mobile compounds in surface soils will be much less. Under some conditions, mobile compounds may move below the surface layer of soil prior to the next application, resulting in no build-up in concentrations in the surface layer of soil as a result of repeated applications.

The conduct of assessments based on concentrations in the surface layer of soil is facilitated by the existence of standard scenarios. The guidance given in the EU registration guidelines (specifying mixing depth, bulk density, and percent of applied reaching the soil) is quite helpful. The existence of more specific climatic and soil scenarios for use with simulation models (*e*.g. as proposed in Chapter 4) would also be useful and should be developed for use in the EU registration process. In addition to affecting downward movement, the selection of climatic and soil conditions in these scenarios could have a small effect on transformation rate if the model uses the Walker corrections for temperature and moisture (these routines are used in PERSIST and VARLEACH, which are described in the chapter on model assessment). As mentioned earlier, the simulation models used in soil concentration assessments will often be the same models used for leaching assessments. However, any model recommended for regulatory use must have an official sponsor responsible for distribution, version control, upgrades, and maintenance. Transformation estimates should be the best information available and field study results, when available, should usually be preferred to laboratory measurements.

The simple model approaches should never be considered as independent cut-off criteria. However, such calculations could trigger additional or field studies, and should only be used as the basis for regulatory decisions in the absence of such studies. Results of the more rigorous simulation models should be considered as adequate replacements for the simple models (assuming agreement between regulators and registrants about the appropriateness of input parameters used in the simulations). Results of well designed field studies conducted under conditions appropriate for the intended use market should also be considered more definitive than modelling predictions.

Figure 1. Procedure for assessing short and long term effects resulting from concentrations of crop protection chemicals in the surface layer of soil following a single application (note that the EU registration guidelines require submission of both instantaneous and time-weighted average concentrations at certain time intervals, even if the value of the initial concentration is sufficient to determine that a use is safe).

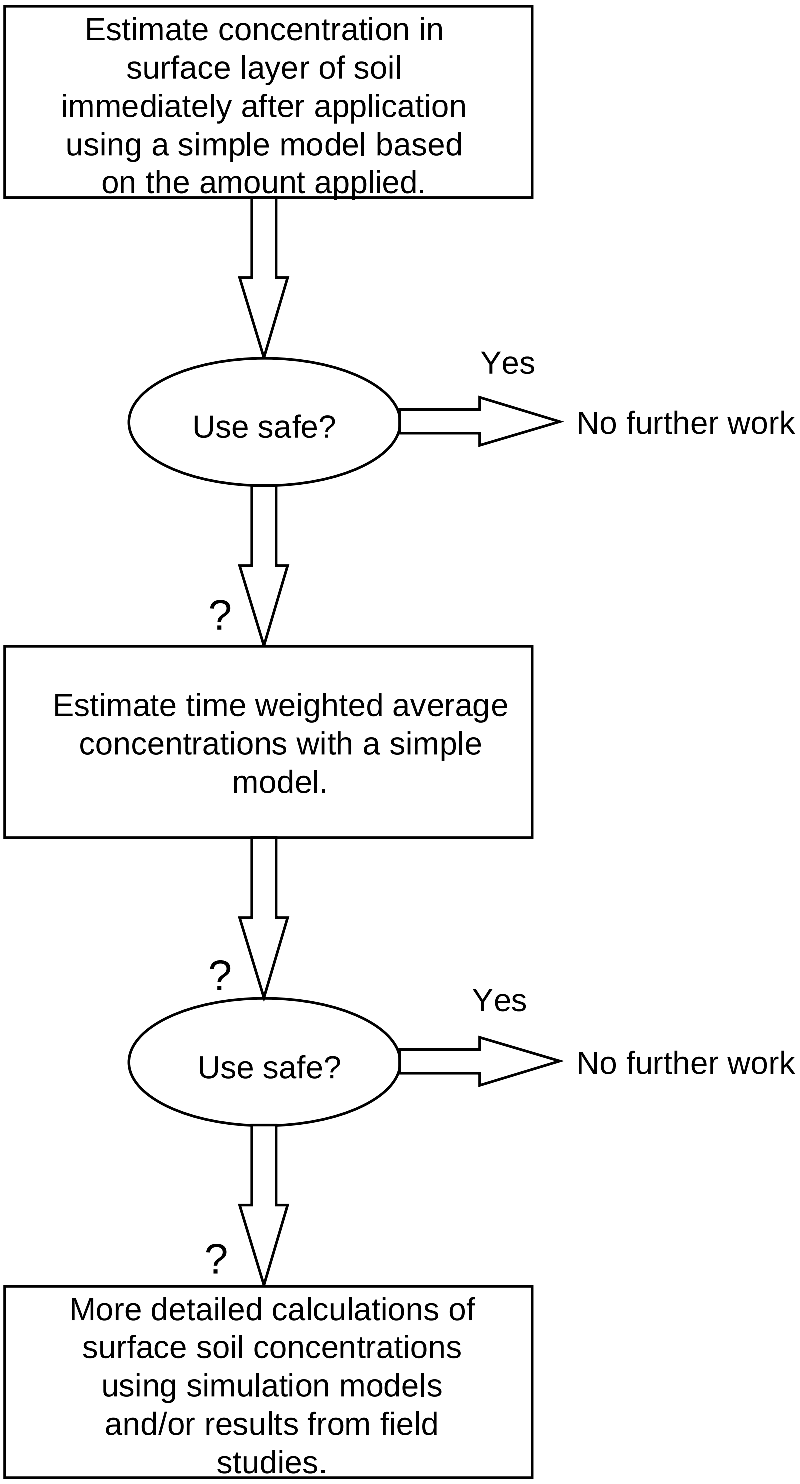

Figure 2. Procedure for assessing short and long term effects resulting from concentrations of crop protection chemicals in the surface layer of soil following multiple applications (note that the EU registration guidelines require submission of both instantaneous and time-weighted average concentrations at certain time intervals, even if the value of the initial concentration is sufficient to determine that a use is safe).

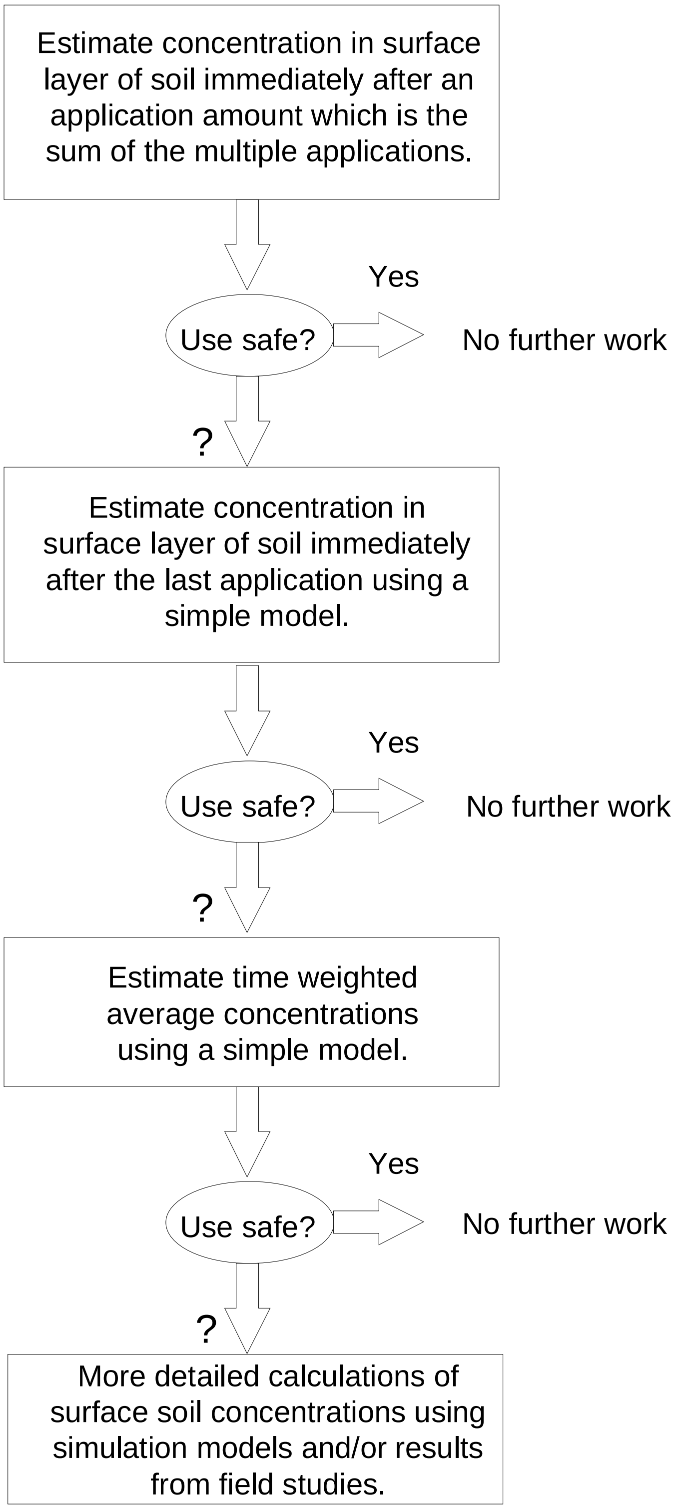

Figure 3. Procedure for assessing long term effects resulting from the build-up of residues of crop protection chemicals in the surface layer of soil.

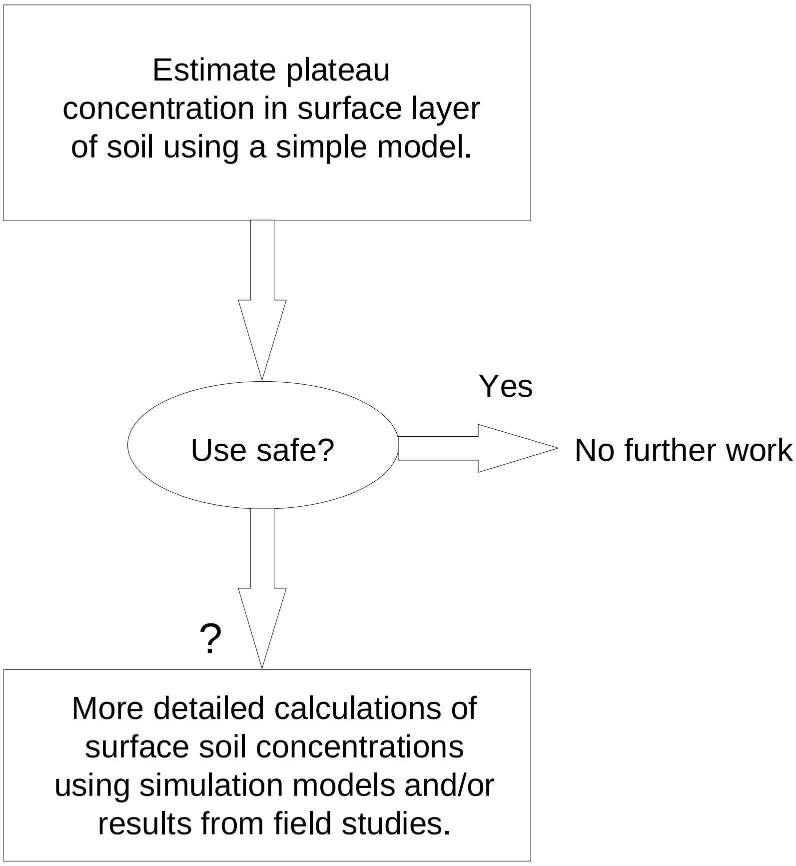

Figure 4. Typical differences between predicted and measured concentration profiles.