PROBABILISTIC CALCULATION OF AQUATIC EXPOSURE VIA DRAINFLOW

1 CONTENTS

2 INTRODUCTION

A literature review and statistical analysis was undertaken to identify the most important factors influencing transport of pesticides to sub-surface drains in agricultural fields. The review encompassed all available field studies on transport of pesticides to subsurface drains undertaken in Europe. The requirements for inclusion of a particular study were regular collection of samples for analysis directly from a drain outfall and the reporting of the maximum concentration and/or seasonal loss of pesticide in drain flow. Studies that assessed leaching through soil coring or where sampling focused on receiving surface waters were excluded. A unique record was assigned to each combination of field site, pesticide and calendar year. In total, reports from 23 studies were accessed from seven countries (Table 1), reporting the leaching of 39 different pesticides. There were 167 unique records for maximum concentration and 97 records for seasonal loss. Maximum concentrations observed during drainage ranged from not detected to 1570 µg/l. Seasonal losses ranged up to 10.6% of the applied amount. Prior to analysis, the maximum observed concentration was standardised to the equivalent value assuming an application of 1 kg a.s. ha^{-1}.

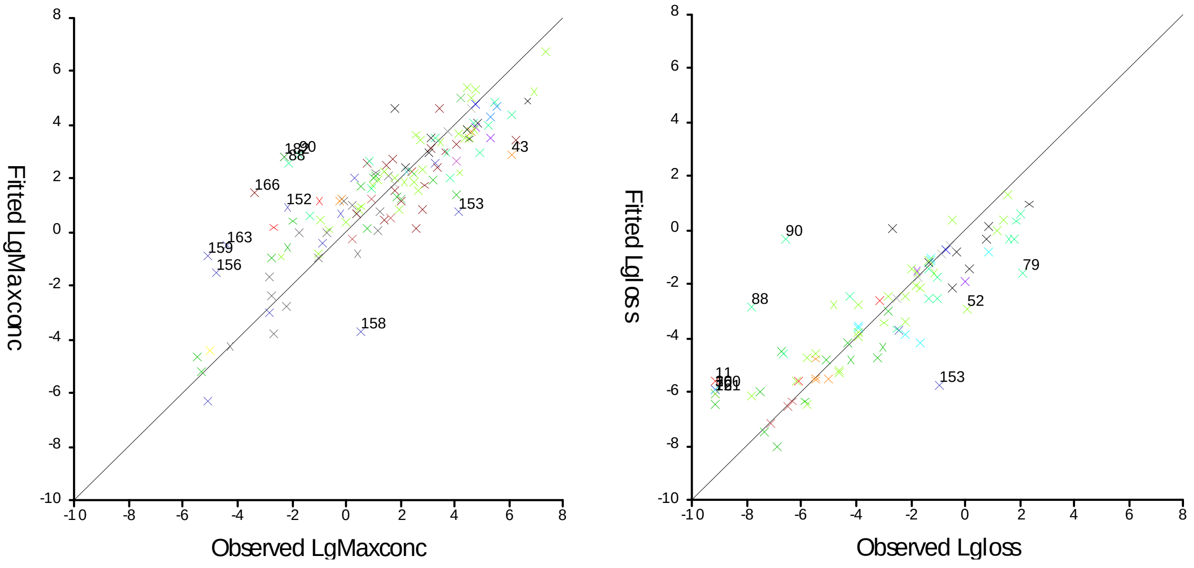
Table 1. **Number of records included in literature study and statistical analysis**

		No. of records	
Country	No. studies	Max. concentration	Seasonal loss
United Kingdom	9	84	61
Germany	4	19	6
Denmark	3	46	7
Netherlands	2	3	0
France	2	0	8
Italy	2	11	11
Norway	1	4	4

Statistical analysis was used to determine which factors affect the maximum concentration and the seasonal loss of pesticides through subsurface drainage. All available data on parameters that could have influenced the leaching of pesticides were extracted from the reports for each study and summarised in a spreadsheet. Taking into account the correlations between observations within one study, and the different levels of variance within the different studies, the appropriate statistical technique to use was residual maximum likelihood. Similar to multiple regression, the method identifies a combination of factors that best explains the values for maximum concentration and seasonal loss (Figures 1 and 2).

Four factors were identified as important influences on both the maximum concentration and total loss of pesticide to drains. These were (1) the time interval between when the pesticide was applied and the occurrence of the first subsequent drainage event; (2) strength of sorption of the pesticide to soil; (3) rate of degradation of the pesticide in soil; and (4) clay content of the soil (this factor is important because it provides a surrogate measure of the relative extent of preferential flow at a site). The design of the drainage system (specifically drain spacing) was found to be an additional factor determining seasonal loss of a pesticide in drainflow.

Figure 1. **Goodness of fit plots for the models for maximum concentration of pesticide in drain flow (left-hand figure) and seasonal loss of pesticide in drainflow (right-hand figure). Model output *vs.* observed values on a 1:1 logarithmic scale.**



2.1 Overview of the model

Based on the statistical analysis, the four factors identified as determining losses via drains are included as primary factors in the model:

1. The model is available for nine scenarios comprising combinations of three soil scenarios (determined primarily based on **clay content**) and three climatic classifications. Scenarios to be run are automatically selected as those relevant to a selected crop type.
2. The initial concentration of pesticide in soil is calculated using crop- and growth stage-specific information on crop interception and accounting for uncertainty in the amount of spray intercepted.
3. The **time interval between application and drainflow** is calculated based on sampling from distributions for the duration, start and end dates of the field capacity period for the respective climate zone. This is the time when the soil profile is fully wetted and any rainfall can be expected to initiate drainflow. The timing of application is also considered to vary within a period that is plus or minus seven days from the target date.
4. The residue of pesticide present in soil at the start of drainflow is calculated based on the initial residue, the time from application to drainage and a **compound-specific degradation rate**. Half-life for the pesticide in soil is sampled from a log-normal distribution based on all available measured values and with an option to either include or exclude uncertainty based on sampling the value from a distribution based on a small number of measurements. Rate of degradation is subsequently corrected for soil temperature on a monthly basis.
5. The proportion of pesticide in soil solution and thus available for transport is calculated by sampling from a log-normal distribution for the **organic carbon partition coefficient** (Koc), a uniform distribution for the Freundlich exponent (nf), and a log-normal distribution for the organic carbon content of the respective soil. The user has the option to include or exclude uncertainty based on sampling Koc from a distribution based on a small number of measurements.
6. Multiple runs of the preferential flow model MACRO 4.3 were used to derive a metamodel that relates the concentration of pesticide in soil solution at the start of drainflow to the total loss of the pesticide in a 10-mm drainage event. The metamodel takes the form of separate quadratic equations for each of the three soil types. The metamodel is run using the input from Step 5 above.
7. The predicted loss of pesticide in 10 mm drainflow is diluted into a ditch by assuming that flow originates from a 1-ha field and is instantaneously mixed into a ditch with dimensions 100 m x 1 m x 0.3 m. The resulting exposure concentration ignores any sorption of pesticide to sediment in the ditch.

2.2 Plan of analysis

Probabilistic risk assessment aims to show the effects of variability and uncertainty on the assessment. Variability is an inherent property of natural systems and cannot be reduced by further measurement. Uncertainty is, crudely, the sum of what we do not know; it includes, for example, sampling bias, measurement error, inadequate descriptions of processes in a model, phenomena which remain unknown and/or unquantified etc.

Methods for propagating uncertainty
Exposure concentrations are calculated using a model coded in MATLAB v8. Selected sources of uncertainty and variability are accounted for in the modelling of exposure. Uncertainty and variability are separated out by 2-D Monte Carlo modelling. Second-order Monte Carlo analysis is useful in cases where it is possible to clearly classify variables as representing either variability or uncertainty. It is particularly helpful in managing parameter or model uncertainty. In first-order Monte Carlo analysis, values are repeatedly sampled from input distributions to produce an output distribution. The distributions or their parameters are estimated and hence subject to sampling error. However, in first-order Monte Carlo we assume them to be known and fixed. Second-order Monte Carlo can overcome this difficulty by explicitly considering parameter uncertainty in the outer loop of the simulation. Output distributions considering variability are then calculated for each value of the parameters in the outer loop. This results in a large number of output distributions and allows to quantify the uncertainty in the result of the 1-D Monte Carlo analysis (e.g. the probability that a particular exposure concentration will occur and the 95% confidence interval around this probability).

Advantages of 2-D Monte Carlo modelling over 1-D modelling:
- The method can separate out uncertainty and variability.
- It can handle model uncertainty in a limited way.

Disadvantages:
- Simulations can take a lot of computer power to run.
- Parameterisation can be difficult.
- Results are difficult to present and explain.
- It does not take account of uncertainty about distribution shape.

Methods for representing dependencies and model uncertainty
In this study, uncertainty in the calculation is expressed using confidence intervals around the median distribution of exposure concentrations. The confidence interval(s) to be reported is a user input. The 95% confidence interval has often been used in communicating results from uncertainty analyses. However, other percentiles can be derived and reported as required.

Basis for assigning distributions as variability and uncertainty
The target prediction is the maximum concentration of pesticide in drainage from fields of the respective soil type in the respective climate zone. Distributed variables related to soil, crop and climate are assumed to encompass inherent variability in the system and are included in the inner (variability) loop of the model. Distributed variables related to the pesticide are assumed to encompass uncertainty associated with sampling the ‘true’ value for a pesticide property and are included in the outer (uncertainty) loop of the model.

3 ENVIRONMENTAL SCENARIOS

3.1 Soils classification

Drained soils comprise approximately 50% of the arable land in England and Wales (data from the SEISMIC database; Hallett et al., 1995). The soil series making up the drained wheat area have been divided into six broad classes using the hydrology of soil types classification. These classes were then ranked according to vulnerability to losses of pesticide in drainflow based on prevalence of preferential flow, organic carbon content and type of drains installed. The three most vulnerable classes were selected for inclusion within the drainage model and a representative soil was selected for each class. All arable and orchard crops are grown on at least one of these three most vulnerable soil types. Simulations that consider those of the three vulnerable scenarios that are relevant to the target crop will be protective of the remaining (less vulnerable) drained arable area of England and Wales. The three classes and representative series are described briefly below. Major properties taken from the SEISMIC database are given in Table 2. The classes are sequential so that soils within the Denchworth class are *a priori* excluded from subsequent classes and so on.

Representative series Denchworth

Clayey soils with a strong inhibition of downwards movement of water which have a soft impermeable layer within 100 cm of the soil surface and a gleyed layer within 70 cm depth. Soils meeting this criteria but with texturally contrasting upper layers were excluded. These soils are drained to remove excess surface water and limit the formation of perched water tables.

Representative series Hanslope

Soils with clayey upper layers with either: (a) significant inhibition of downwards movement of water and which have a slowly permeable layer and a gleyed layer within 100 cm of the soil surface; or (b) prolonged seasonal saturation and a gleyed layer within 40 cm of the soil surface as a result of shallow groundwater. Soils in category (a) form by far the largest part of this class. Drains are installed to (a) remove excess surface water and limit the formation of perched water tables; or (b) control a shallow groundwater table.

Representative series Brockhurst

Soils with clayey lower layers and lighter textured upper layers with either: (a) significant inhibition of downwards movement of water and which have a slowly permeable and a gleyed layer within 100 cm of the soil surface; or (b) prolonged seasonal saturation and a gleyed layer within 40 cm of the soil surface as a result of shallow groundwater. Soils in category (a) form by far the largest part of this class. Drains are installed to (a) remove excess surface water; or (b) control a shallow groundwater table.

Table 2. Selected properties of the five soils (all properties taken from SEISMIC)

	Depth interval (cm)	% organic carbon	% sand	% silt	% clay	Bulk density (g/cm^3)	pH
Denchworth series							
Horizon 1	0-20	2.9	17	40	43	1.17	6.3
Horizon 2	20-50	1.2	6	30	64	1.26	6.9
Horizon 3	50-70	0.8	5	31	64	1.31	7.0
Horizon 4	70-100	0.4	6	36	58	1.40	7.4
Hanslope series							
Horizon 1	0-25	2.9	30	32	38	1.18	7.7
Horizon 2	25-50	0.9	22	36	43	1.38	8.2
Horizon 3	50-65	0.5	20	33	47	1.45	8.3
Horizon 4	65-100	0.4	14	45	41	1.44	8.3
Brockhurst series							
Horizon 1	0-25	2.3	32	42	26	1.26	6.4
Horizon 2	25-45	0.6	30	44	26	1.49	6.4
Horizon 3	45-70	0.3	14	40	46	1.48	6.7
Horizon 4	70-100	0.2	7	48	45	1.51	7.5

3.2 Climatic classification

The time between application of a pesticide and drainflow commencing is an important influence on losses of pesticide to drains. The dates and duration of the period when the soil is at field capacity was considered the best indicator of this influence. Duration of field capacity was thus used to generate climatic scenarios for use in drainage modelling. Three climatic categories were defined to cover the main areas of arable cultivation in England and Wales:

Dry climate	Soil at field capacity for less than 125 days per year on average
Medium climate	Soil at field capacity for between 125 and 165 days per year on average
Wet climate	Soil at field capacity for between 165 and 195 days per year on average

Agriculture in areas with >195 days at field capacity is dominated by non-arable farming systems. Arable cultivation may still be present in these areas, but is more sparsely distributed.

3.3 Selection of relevant scenarios

The drainage model is run for up to three soils (Denchworth, Hanslope and Brockhurst) and three climate scenarios (dry, medium, and wet). The table below specifies which of the soils are relevant for each crop. The soils are combined with all three climate scenarios.

	Denchworth	Hanslope	Brockhurst
fodder peas		X	X
maize	X	X	X
potatoes		X	X
sugar beet		X	X
winter oilseed rape	X	X	X
spring wheat		X	X
winter wheat	X	X	X
spring barley		X	X
winter barley	X	X	X
winter rye	X	X	X

4 DOCUMENTATION FOR THE DENCHWORTH / WET SCENARIO

The documentation below details the model for the Denchworth / wet scenario to exemplify the different components of the model.

4.1 Uer inputs

- Crop type and growth stage.
- Application rate (g a.s./ha)
- Application date
- DT50 at pF2 and 20^{o}C (up to 30 available values)
- Koc and nf pairs (up to 30 available values)

4.2 Selection of application rate for interception by the crop

Becker et al. (1999) give means and standard deviations of percentages of ground cover for a number of crops at different growth stages. These were assumed to be equal to % intercepted and normally distributed. The user selects the crop and the mean and stdev % ground cover are read from a lookup table (Table 3). The % interception is then sampled from a normal distribution truncated at the 10th percentile and 95th percentile. Where min < 10% of the mean, the minimum is set to 10% of the mean. Where max > 100, this is set to 100. Example: Winter wheat BBCH 11-19: mean interception = 19.3%, stdev = 10.7, min = 5.6, max = 33.0. Winter barley BBCH 11-19: mean interception = 15.4%, stdev = 12.7, min = 1.5, max = 31.7.

Corrected application rate (g/ha) = (100 minus sampled % interception)/100 x application rate

Table 3. Values for crop interception used within the model

	mean	**stdev**	**min**	**max**
fodder peas BBCH 10-15	18.8	13.8	1.9	36.5
fodder peas BBCH 16-21	29	25.1	2.9	61.2
fodder peas BBCH 22-29	33.4	23.45	3.3	63.5
fodder peas BBCH 30-39	37.8	21.8	9.9	65.7
fodder peas BBCH 40-50	44.45	23.4	14.5	74.4
fodder peas BBCH 51-59	51.1	25	19.1	83.1
fodder peas BBCH 61-69	67.7	21.4	40.3	95.1
fodder peas BBCH 71-85	70.3	22.7	41.2	99.4
maize BBCH 12-14	7.1	5	0.7	13.5
maize BBCH 15	11.9	4.9	5.6	18.2
maize BBCH 16	18.4	16.2	1.8	39.2
maize BBCH 17	16.5	9.6	4.2	28.8
maize BBCH 18	22.7	10.2	9.6	35.8
maize BBCH 19	31.9	18.5	8.2	55.6
maize BBCH 20-29	30.85	16.6	9.6	52.1
maize BBCH 30-33	29.8	14.7	11.0	48.6
maize BBCH 34-49	41.7	15.4	22.0	61.4
maize BBCH 50-59	61.1	13.1	44.3	77.9
maize BBCH 61-69	76.3	10.8	62.5	90.1
maize BBCH 71-89	82.4	11.8	67.3	97.5
potatoes BBCH 10-18	8.7	9.1	0.9	20.4
potatoes BBCH 21-29	30.4	15.7	10.3	50.5
potatoes BBCH 31-39	37.4	16.2	16.6	58.2
potatoes BBCH 40-50	54.3	13.25	37.3	71.3
potatoes BBCH 51-55	71.2	10.3	58.0	84.4
potatoes BBCH 61-89	74	11.2	59.6	88.4
potatoes BBCH 91-99	35	20.6	8.6	61.4
spring barley BBCH 13-17	31.6	2.4	28.5	34.7
spring barley BBCH 21-29	36.3	20.3	10.3	62.3
spring barley BBCH 30-33	64	19.8	38.6	89.4
spring barley BBCH 35-49	76.4	22.7	47.3	100.0
spring barley BBCH 51-59	80.1	18.4	56.5	100.0
spring barley BBCH 61-69	87.1	11.3	72.6	100.0
spring barley BBCH 71-92	90.4	8.5	79.5	100.0
spring wheat BBCH 11-19	19.3	10.7	5.6	33.0
spring wheat BBCH 21-29	36.7	8.2	26.2	47.2
spring wheat BBCH 30-33	59.1	12.2	43.5	74.7

spring wheat BBCH 35-49	73.9	17.8	51.1	96.7
spring wheat BBCH 51-59	73.6	13.7	56.0	91.2
spring wheat BBCH 61-69	89.3	11.9	74.0	100.0
spring wheat BBCH 71-92	86.6	5.2	79.9	93.3
sugar beet BBCH >49	98.1	5.2	91.4	100.0
sugar beet BBCH 10	1.6	1	0.3	2.9
sugar beet BBCH 11	2.3	1.4	0.5	4.1
sugar beet BBCH 12	4.7	2.8	1.1	8.3
sugar beet BBCH 13	13.1	5.8	5.7	20.5
sugar beet BBCH 14	11.3	5.8	3.9	18.7
sugar beet BBCH 15	12.9	5.2	6.2	19.6
sugar beet BBCH 16	19.1	8.8	7.8	30.4
sugar beet BBCH 17	14.5	6.2	6.6	22.4
sugar beet BBCH 18	23	10.8	9.2	36.8
sugar beet BBCH 19	39.5	9	28.0	51.0
sugar beet BBCH 20-30	42.55	10.40	29.2	55.9
sugar beet BBCH 31	45.6	11.8	30.5	60.7
sugar beet BBCH 33	58.9	13.9	41.1	76.7
sugar beet BBCH 35	64	8.4	53.2	74.8
sugar beet BBCH 37	75	6.9	66.2	83.8
sugar beet BBCH 38	90	0	90.0	90.0
sugar beet BBCH 39	83.9	6.8	75.2	92.6
sugar beet BBCH 43-49	98.1	2.8	94.5	100.0
winter barley BBCH 11-19	15.4	12.7	1.5	31.7
winter barley BBCH 21-29	41.2	22.2	12.7	69.7
winter barley BBCH 30-33	61.8	20.3	35.8	87.8
winter barley BBCH 34-49	79.4	16.5	58.3	100.0
winter barley BBCH 51-59	75.5	15.8	55.3	95.7
winter barley BBCH 61-69	89.8	11.6	74.9	100.0
winter barley BBCH 71-89	89.3	11.7	74.3	100.0
winter barley BBCH 71-90	86	8.3	75.4	96.6
winter oilseed rape BBCH 10-11	6.6	6.2	0.7	14.5
winter oilseed rape BBCH 12	8.5	4.6	2.6	14.4
winter oilseed rape BBCH 13	9.8	7.5	1.0	19.4
winter oilseed rape BBCH 14	19	17.8	1.9	41.8
winter oilseed rape BBCH 15	34.1	24.1	3.4	65.0
winter oilseed rape BBCH 16	33.7	19.8	8.3	59.1
winter oilseed rape BBCH 17	38.8	18.7	14.8	62.8
winter oilseed rape BBCH 18	53.9	21.5	26.3	81.5
winter oilseed rape BBCH 19	55.8	18.7	31.8	79.8
winter oilseed rape BBCH 20-29	61.2	19.9	35.7	86.7
winter oilseed rape BBCH 31-39	67.6	15.3	48.0	87.2
winter oilseed rape BBCH 40-50	73.75	13.45	56.5	91.0
winter oilseed rape BBCH 51-59	79.9	11.6	65.0	94.8
winter oilseed rape BBCH 61-69	77.1	15.2	57.6	96.6
winter oilseed rape BBCH 71-89	88.9	9.7	76.5	100.0
winter oilseed rape BBCH 92	90.5	7.4	81.0	100.0
winter rye BBCH 13-16	14.5	4.6	8.6	20.4
winter rye BBCH 21-29	31.5	13	14.8	48.2
winter rye BBCH 30-33	52.8	14.1	34.7	70.9
winter rye BBCH 35-49	64.8	14.3	46.5	83.1
winter rye BBCH 51-59	74.7	15.8	54.5	94.9

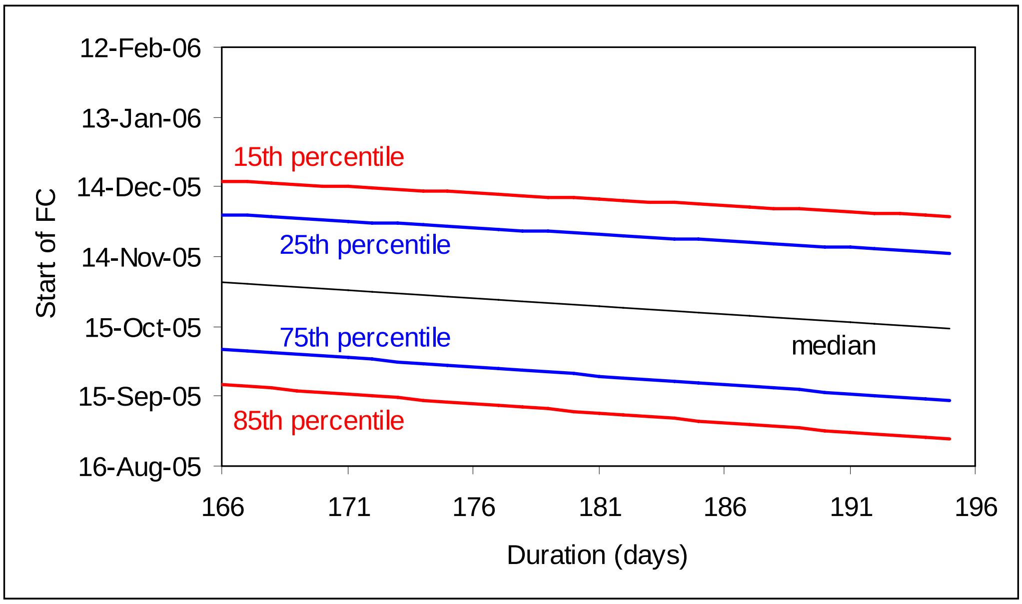
winter rye BBCH 61-69	80.2	12.4	64.3	96.1
winter rye BBCH 71-92	77	15.1	57.6	96.4
Winter wheat BBCH 11-19	19.3	10.7	5.6	33.0
Winter wheat BBCH 21-29	40.8	18.9	16.6	65.0
Winter wheat BBCH 30-33	59.3	17.9	36.4	82.2
Winter wheat BBCH 34-49	74.8	14.9	55.7	93.9
Winter wheat BBCH 51-59	77.1	14.2	58.9	95.3
Winter wheat BBCH 61-69	76.3	22	48.1	100.0
Winter wheat BBCH 71-97	85.5	10.3	72.3	98.7

4.3 Application date

The user enters a target application date and the model then samples from a uniform distribution between user input ± 7 days.

4.4 Time at which the field capacity period starts

It is assumed that drainflow starts at the time when the soil reaches field capacity (FC). The analysis is based on data from the National Soils Resources Institute for the median, 25th and 75th percentile dates for return to field capacity and end of the field capacity period. These data are available for England and Wales expressed on a 5 x 5 km grid. For the wet scenario, the duration of the field capacity period ranges from166 to195 days. A duration is sampled from a uniform distribution. The start of the field capacity period can be calculated from the duration of the period.



The 25th percentile start date (in days relative to 31 December) is calculated from:
Days from 31 Dec = – 0.5707 duration + 65.868

The median start date (in days relative to 31 December) is calculated from:
Days from 31 Dec = – 0.6741 duration + 53.737

The 75th percentile start date (in days relative to 31 December) is calculated from:
Days from 31 Dec = – 0.7674 duration + 40.708

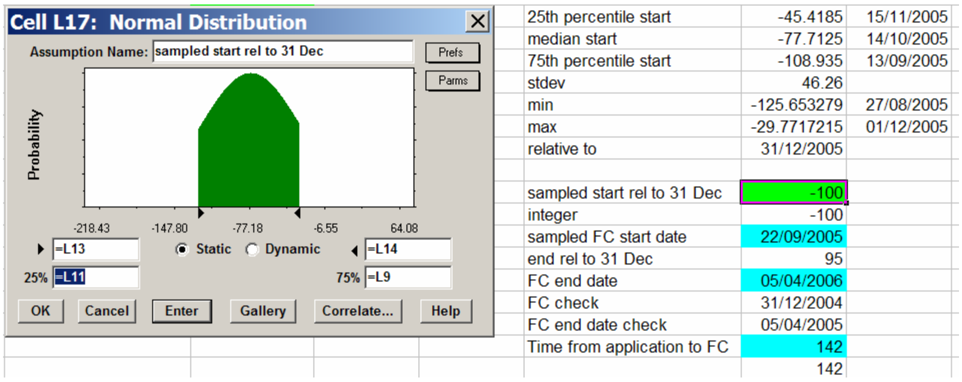
The 25th percentile, median and 75th percentile date (dd/mm/yyyy) on which field capacity starts is calculated as
31/12 in the year of application + the calculated no of days.

It is assumed that the number of days relative to 31 Dec is normally distributed. The standard deviation can then be calculated as: (75th percentile-median)/0.675. The 15th and 85th percentiles are calculated from the mean and standard deviation.

Example: Sampled duration = 175:

25th percentile start	-34.0	26/11/2005
median start	-64.2	27/10/2005
75th percentile start	-93.6	28/09/2005
stdev	43.5	
15th percentile start	-109.3	12/09/2005
85th percentile start	-19.2	11/12/2005

A start date (in days from 31 Dec) is then sampled from a normal distribution truncated at the 15th and 85th percentile. The end date of the field capacity period is calculated from the sampled duration + the sampled start date.



Assumption Name: sampled start rel to 31 Dec

=L13

● Static ○ Dynamic

=L14

25% =L11

75% =L9

25th percentile start	-45.4185	15/11/2005
median start	-77.7125	14/10/2005
75th percentile start	-108.935	13/09/2005
stdev	46.26	
min	-125.653279	27/08/2005
max	-29.7717215	01/12/2005
relative to	31/12/2005	
sampled start rel to 31 Dec	-100	
integer	-100	
sampled FC start date	22/09/2005	
end rel to 31 Dec	95	
FC end date	05/04/2006	
FC check	31/12/2004	
FC end date check	05/04/2005	
Time from application to FC	142	
	142	

4.5 Time between application and the drainflow event

- If the application date is after the end of the previous field capacity period and 3 or more days before the start of the next field capacity period, then the time between the sampled application date and the start of drainflow is:

  start of FC date minus application date

- If the application date is less than three days before the start of the next field capacity period, then the time between the sampled application date and the start of drainflow is:

  3 days

- If the application date is between the start and end of the field capacity period, then the time between the sampled application date and the start of drainflow is:

  3 days

Examples:

End of FC period 1	Start of FC period 2	End of FC period 2	Application date	Time between application & onset of drainflow	Comment
14/03/2005	20/09/2005	14/03/2006	01/03/2005	3	earlier than end of FC period 1
			01/05/2005	142	time from 01/05/2005 to 20/09/2005
			18/09/2005	3	less than 3 days before start of FC 2
			01/10/2005	3	in FC period 2
			01/11/2005	3	in FC period 2

4.6 Degradation

DT50 in soil is an important input to the model, determining extent of degradation of residues in the interval between application and initiation of drainage. The model assumes that degradation follows first-order kinetics.

The user enters a number of data for the DT50 value at reference moisture and temperature (pF2 and 20°C). (log10) DT50 is assumed to be normally distributed (normal distribution of log(10)DT50 = lognormal distribution of DT50). This distribution shape is based on the review of literature reported by Beulke et al. (2005). A value is sampled from a normal distribution with mean = mean of all log(10)DT50 and stdev = stdev of all log(10)DT50. The user can choose to either include or exclude uncertainty associated with assigning a distribution to DT50 based on a small number of measurements (see Section 4.9). The distribution is truncated at the 2.5th percentile and 97.5th percentile. The DT50 is calculated from the sampled value as $10^{\wedge \log DT50}$. A degradation rate is calculated from the DT50 as ln(2)/DT50.

The sampled degradation rate must be corrected for the actual soil temperature between the time of application and the drainflow event. Monthly averages of soil temperature in 0-4 cm were calculated for a Denchworth run for 16 years + 2 years pre-run with a dry weather scenario (Brown et al., 2004).

	average soil temp
Jan	6.8
Feb	6.4
Mar	7.5
Apr	9.7
May	12.1
Jun	14.3
Jul	15.3
Aug	13.9
Sep	13.0
Oct	11.6
Nov	7.0
Dec	6.1

The degradation rate is multiplied with a correction factor which is calculated as follows:

$$factor = 2.2^{\left(\frac{av.\ temp\ this\ month - 20}{10}\right)}$$

	factor
Jan	0.3522
Feb	0.3412
Mar	0.3736
Apr	0.4438
May	0.5359
Jun	0.6367
Jul	0.6893
Aug	0.6175
Sep	0.5754
Oct	0.5159
Nov	0.3583
Dec	0.3331

- If the time between application and the start of the drainflow event is 30 days or less, then the correction factor for the month in which application is made is selected. The degradation rate is multiplied with this factor.
- If the time between application and the start of the drainflow event is longer than 30 days, then the correction factors are averaged between the month in which application is made and the month in which the field capacity period starts. The degradation rate is multiplied with the average factor.

Example:

Start of FC period	Application date	Time from application to start of drainflow	Correction factor	Comment
20/09/2005	01/05/2005	142	0.6110	Average May-September
20/09/2005	18/09/2005	3	0.5754	Factor for September
20/09/2005	01/10/2005	3	0.5159	Factor for October

	factor
Jan	0.3522
Feb	0.3412
Mar	0.3736
Apr	0.4438
May	0.5359
Jun	0.6367
Jul	0.6893
Aug	0.6175
Sep	0.5754
Oct	0.5159
Nov	0.3583
Dec	0.3331

Soil moisture content fluctuates both with depth in the profile and in response to rainfall. The MACRO model predicts that moisture contents in heavy clay soils are close to or wetter than pF2 for most of the year, so no correction of rate of degradation for soil moisture content has been included in the model.

4.7 Aerial mass at time of drainflow event

The corrected degradation rate from section 4.6.
The corrected application rate from Section 4.2.
The time between application and drainflow event are taken from Section 4.5.

$$Aerial\ mass = A\ e^{-time \times k}$$

with
aerial mass = aerial mass left at time of drainflow event (g/ha)
A = corrected application rate (g/ha)
time = time between application and drainflow event (days)
k = corrected degradation rate (days^{-1})

To convert to mg/m^2:
aerial mass (g/ha) x 1000/10000 = aerial mass (mg/m^2)

Soil layer = 4 cm deep
1 m^2 area = 10000 cm^2 x 4 cm = 40000 cm^3 soil volume in the 4-cm layer
bulk density = 1.17 g/cm^3
40000 cm^3 = 46800 g = 46.8 kg soil

Divide mg/m^2 pesticide by 46.8 kg to derive mg pesticide per kg soil. This is the soil residue at the time of the drainflow event.

4.8 Sorption

Extent of sorption in soil determines the availability of pesticide residues for transport in drainflow. The model assumes that sorption is characterised by a Freundlich isotherm.

The user enters measured pairs of Freundlich coefficients normalised to organic carbon (Koc) and Freundlich exponents (nf). Each of the measurements of nf is sampled with equal probability. The model does not assign a distribution to nf as there is no literature information to support selection of a distribution shape.

(log10) Koc is assumed to be normally distributed (normal distribution of log(10)Koc = lognormal distribution of Koc). This distribution shape is based on the review of literature reported by Beulke et al. (2005). The mean and standard deviation of the measured log(10)Koc values are taken as an estimate for the mean and standard deviation of the underlying normal distribution. The user can choose to either include or exclude uncertainty associated with assigning a distribution to Koc based on a small number of measurements (see Section 4.9). The distributions are truncated at the 5th percentile and 95th percentile. Values for the number of iterations in the outer and inner loops of the model (X and Y) are user inputs entered in the Calculation Parameters screen.

The calculation of sorption also takes account of the distribution in organic carbon content for the soil series being simulated (based on information on the mean and standard deviation from the SEISMIC database; Hallett et al., 1995). The % organic carbon content is sampled from a normal distribution truncated at the 10th percentile and the 90th percentile:

Soil	Mean	Stdev	Min	Max
Denchworth	2.9	1.2	1.362	4.438
Hanslope	2.9	1.8	0.593	5.207
Brockhurst	2.3	1.1	0.890	3.710

The Freundlich coefficient (Kf value) is then calculated as

Kf = Koc x % organic carbon / 100

4.9 Inclusion of sampling uncertainty for Koc and DT50

Sorption to soil (Koc) and degradation half-life in soil (DT50) are two of the most sensitive input parameters for estimating transport of a pesticide in drainflow. Selection of a value for Koc and DT50 is uncertain because (1) measurements for different soil types fall within a distribution and selection of the ‘correct’ value for a specific location is thus uncertain and (2) only a small number of measured data are typically available, so the distribution of either Koc or DT50 is itself uncertain.

Two options are available to treat uncertainty around the value for Koc and DT50.

- If you choose NOT to include sampling uncertainty for Koc and DT50, then only the first type of uncertainty will be included within the model. A most likely estimate of the log-normal distribution for either Koc or DT50 will be fitted and a value from that single distribution is randomly sampled at each iteration within the uncertainty (outer) loop of the model.
- If you choose to INCLUDE sampling uncertainty for Koc and DT50, then both types of uncertainty will be included within the model. The methodology that is used was proposed by Vose (2000) to account for uncertainty in sampling from distributions based on small datasets. First, the most-likely estimate of the mean and variance is calculated for the log-normal distribution fitted to either Koc or DT50. The mean and variance are then assumed to be distributed and uncertain. At each iteration within the uncertainty (outer) loop of the model, a DIFFERENT, plausible distribution is generated and a single value for Koc or DT50 is randomly sampled from that distribution.

4.10 Availability of the pesticide in soil water

This is calculated from the sampled values using an iterative procedure (i.e. after running the first part of the model). This is because an analytical solution does not exist.

Availability (%) = mass in soil solution (mg/kg) in percent of total mass (mg/kg)

$$Mass\ in\ solution = \frac{\theta}{\rho} C$$

$$Total\ mass = \frac{\theta}{\rho} C + S$$

$$Total\ mass\ = \frac{\theta}{\rho} C + Kf\ C^{\ nf} = \frac{\theta}{\rho} C \left(1 + \frac{\rho}{\theta} Kf^{\,nf-1} \right)$$

$$Availability\ = \frac{1}{1 + \frac{\rho}{\theta} Kf\ C^{\ nf-1}} \times 100$$

where

θ = water content in micropores in 0-4 cm = 0.39757 L/L (fixed value)
ρ= bulk density in 0-4 cm = 1.17 kg/L (fixed value)
C = concentration in solution (mg/L)
S = sorbed amount (mg/kg)
Kf = Freundlich sorption coefficient (L kg^{-1})
nf = Freundlich exponent (-)

Step 1: Calculate C

The total mass is the soil residue at the start of the event in mg/kg (forecast 'soil residue at time of FC'). For each iteration (separate Kf and nf), the equation

$$Total\ mass\ = \frac{\theta}{\rho} C + Kf\ C^{\ nf}$$

is solved. This is achieved by iteratively finding a value for C that results in the right hand side of the equation being equal to the left.

Example: soil residue = 0.6738. Kf = 2.85, nf = 0.90. The value for C that results in the right hand side of equation being equal to the left is 0.1812.

$$0.6738\ = \frac{0.3976}{1.17} 0.1812 + 2.85 \times 0.1812^{\ 0.90}$$

Step 2: Calculate availability

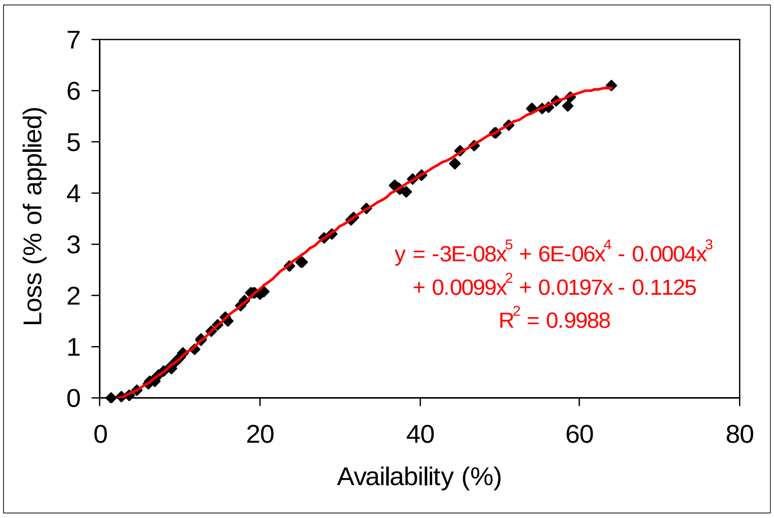
$$Availability\ = \frac{1}{1 + \frac{\rho}{\theta} Kf\ C^{\ nf-1}} \times 100$$

In this example

$$Availability\ = \frac{1}{1 + \frac{1.17}{0.3976} 2.85 \times 0.1812^{\ 0.90-1}} \times 100 = 9.14\%$$

4.11 Loss of the pesticide in drainage water

The amount of pesticide present at the time of the event in g/ha is an output of the first part of the model. The percentage of pesticide lost in drainflow is calculated from a relationship between % loss and %availability:



Example: availability = 9.14%, loss = 0.629%.

0.629% of 315.34 g/ha = 1.98 g/ha.

4.12 Concentration of the pesticide in a standard ditch

The pesticide is applied to a field 100 m wide by 100 m long (1 ha area) The pesticide is assumed to be lost in 10 mm drainflow. This corresponds to 100,000 L flow from a 1-ha field. The drainflow is discharged into a ditch 1-m wide and 30-cm deep that runs alongside one edge of the field. The volume of this ditch is 100 m x 1 m x 0.3 m = 30 m^3 = 30,000 L. The pesticide is thus diluted in a total volume of 130,000 L.

Example: 1.98 g lost from a 1-ha field / 130000 L water = 1.526 x 10^{-5} g L^{-1} = 15.26 µg L^{-1}.

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