PROBABILISTIC CALCULATION OF AQUATIC EXPOSURE VIA DRAINFLOW

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1 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}.

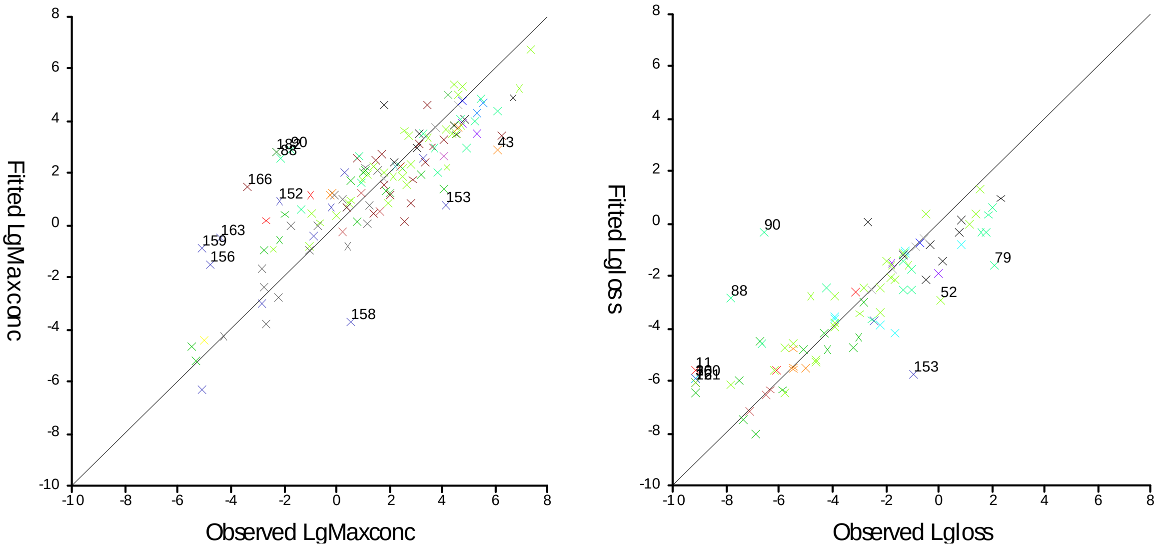
Table 1. Number of records included in literature study and statistical analysis

		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 (Figure 1).

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.**



1.1 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 twelve scenarios comprising combinations of four 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**. When multiple applications are made, the residue just before the last application is calculated and this mass can be added to the amount applied at the last treatment. The half-life for the pesticide in soil is sampled from a distribution based on all available measured values. The rate of degradation is subsequently corrected for soil temperature on a monthly basis. Interactions between degradation and sorption or between degradation and soil pH can be accounted for.
5. The proportion of pesticide in soil solution and thus available for transport can be calculated based on a model assuming instantaneous sorption equilibrium. In this case, the **organic carbon partition coefficient** (Koc) is sampled from a log-normal distribution. A uniform distribution is assumed for the Freundlich exponent (nf), and a log-normal distribution for the organic carbon content of the respective soil. Uncertainty based on sampling Koc from a distribution based on a small number of measurements is included. Alternatively, time-dependent sorption can be modelled. In this instance, parameters for a two-site sorption model must be entered. Each

combination of five model parameters derived from the same experiment is sampled with equal probability. Users also have the option to take into account interactions between sorption and degradation or between sorption and soil pH.

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 regression equations for each of the four soil types. The metamodel is run using the input from the Steps 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.

1.2 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. 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 inner 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 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 variability between experiments and soils and these are also included in the inner loop of the model. Uncertainty based on sampling pesticide properties from a distribution based on a small number of measurements is accounted for in the outer loop of the model. Interception of the pesticide by the crop is uncertain and this included in the outer (uncertainty) loop of the model.

2 ENVIRONMENTAL SCENARIOS

2.1 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 four 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 four most vulnerable soil types. Simulations that consider those of the four vulnerable scenarios relevant to the target crop will be protective of the remaining (less vulnerable) drained arable area of England and Wales.

Probabilistic exposure assessments for the UK situation described by Brown et al. (2004) include a further soil class represented by Quorndon series. These are relatively permeable soils with a gleyed layer within 40 cm of the soil surface because of shallow groundwater. These soils are drained to control the shallow groundwater table. Webfram calculates the loss via drains for each of the soils from the availability of the pesticide in soil solution based on a soil-specific regression equation, based on the results of simulations with the leaching model MACRO. A universally valid regression line could not be derived for the Quorndon soil and it was not possible to include this soil directly in the Webfram tool. Simulations with MACRO indicated that the concentration in the ditch arising from losses via drainflow will be negligible for the Quorndon soil class for application rates up to 2 kg/ha (<0.0005 ug/L). These negligible concentrations are included in summary statistics at the end of the simulations.

The four classes and representative series implemented in Webfram 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.

Table 2. Selected properties of the four 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
Clifton series							
Horizon 1	0-25	3.1	50	30	20	1.20	5.9
Horizon 2	25-40	0.5	52	31	17	1.52	6.2
Horizon 3	40-75	0.4	38	32	30	1.55	6.8
Horizon 4	77-100	0.2	36	32	32	1.64	7.2

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.

Representative series Clifton

Medium loamy and silty soils with either: (a) significant inhibition of downward movement of water, and that have a slowly permeable and a gleyed layer within 100 cm of the soil surface; (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 either to remove excess surface water, or to control a shallow groundwater table.

2.2 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.

2.3 Selection of relevant scenarios

The drainage model is run for up to four soils (Denchworth, Hanslope, Brockhurst and Clifton) and three climate scenarios (dry, medium, and wet). Table 3 specifies which of the soils are relevant for each crop. The soils are combined with all three climate scenarios.

Table 3. Relevant combinations of crops and locations included in Webfram

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

3 DOCUMENTATION FOR THE DENCHWORTH / WET SCENARIO

3.1 User selections

The user has the option to make the following selections:

- Single or multiple application
- Instantaneous sorption equilibrium or time-dependent sorption
- Inclusion of dependencies between sorption, degradation and pH

3.2 User inputs

- Crop type and growth stage.
- Application rate (g a.s./ha)
- Application date
- Interval between applications (where applicable)
- DT50 at pF2 and 20^{o}C (instantaneous sorption) and soil pH (where applicable)
- Q10 (-)
- Koc and nf pairs (instantaneous sorption) and soil pH (where applicable)
- The five parameters of the time-dependent sorption model (where applicable)

3.3 Application details and residual mass

<u>Single application per season</u>

The user enters the application rate and a target application date. The model samples from within ± 7 days of the target date using a uniform distribution.

<u>Multiple application of one substance per season</u>

Webfram calculates losses via drainflow after a single application. The residual mass following multiple applications of the same substance within a season should be added to the rate of the last application before calculating losses via drainage. The user has the option to calculate the residual mass outside Webfram or using an add-on to the model.

The Webfram add-on calculates the mass of pesticide present just before the last application, accounting for any carry-over of previously applied pesticide based on first-order degradation kinetics. The user must enter the rate of each application, the date of the first application and the interval between the applications. The crop growth stage at each application must be selected. A mean value for interception by the crop is used to correct each application rate (see Table 4). The user must also specify a single DT50 value (e.g. the geometric mean of all available DT50 values) and a Q10 value for correction of the DT50 value for temperature within each interval between the applications.

The simulation of drainflow losses only after the last application will not give conservative estimates where the first application is within the field capacity period and the last application occurs after the field capacity period ends. The onset of the drainflow event is set to a default of 3 days for applications within the field capacity period whereas there are several months between applications just after the end of the field capacity period in spring and the onset of drainflow in the following autumn. The end dates of the field capacity period are sampled from distributions within Webfram (see below). The latest possible end dates are 11 May, 31 May and 14 June for the dry, medium and wet weather scenarios, respectively. An alternative approach must be followed where at least one application is made before these dates and at least one application is made after these dates:

1. Simulate concentrations in the ditch arising from losses via drainflow for the first application with the Webfram drainage module;
2. Simulate the mass remaining in soil just before the second application using the multiple applications tool (set no of applications to 2);
3. Add the residual mass to the rate for the second application and simulate concentrations in the ditch arising from losses via drainflow with the Webfram drainage module;
4. Repeat this procedure for all subsequent applications;
5. Report the largest of the concentrations calculated for the various applications.

3.4 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 its growth stage at the time of application from a drop-down menu. The % interception at the last application is sampled from a normal distribution with the mean and standard deviation given in Table 4, 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 4. Values for crop interception used within the model

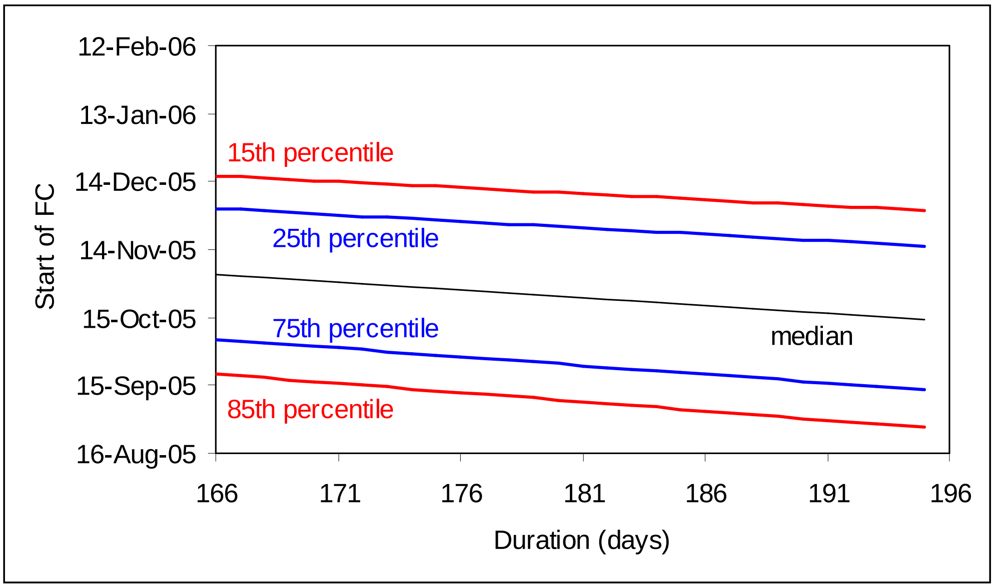
	mean	stdev	min	max
fodder peas BBCH 10-15	18.8	13.8	1.9	36.5
fodder peas BBCH 16-21	29	25.1	2.9	61.2
fodder peas BBCH 22-29	33.4	23.45	3.3	63.5
fodder peas BBCH 30-39	37.8	21.8	9.9	65.7
fodder peas BBCH 40-50	44.45	23.4	14.5	74.4
fodder peas BBCH 51-59	51.1	25	19.1	83.1
fodder peas BBCH 61-69	67.7	21.4	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

3.5 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

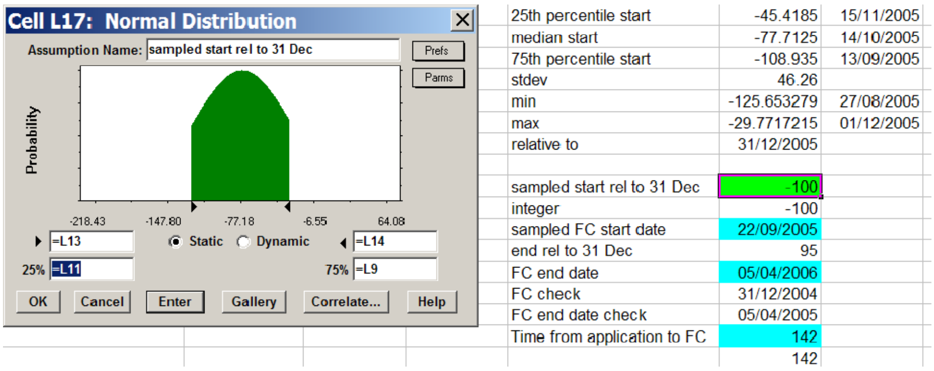
The 25th percentile, median and 75th percentile date (dd/mm/yyyy) on which field capacity starts is calculated as 31/12 in the year of application + the calculated no of days.

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	

3.6 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

3.7 Degradation

DT50 in soil is an important input into the model, determining extent of degradation of residues in the interval between application and initiation of drainage. There are two options for the simulation of degradation in Webfram:

Degradation in the case of instantaneous sorption

The total mass of pesticide in the soil after application is assumed to follow first-order kinetics if sorption is considered to be at instantaneous equilibrium. The user enters a number of data for the DT50 value at reference moisture and temperature (pF2 and 20°C) from standard aerobic degradation experiments. (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 distribution is truncated at the 2.5th percentile and 97.5th percentile. The DT50 is calculated from the sampled value as $10^{\wedge \log \mathrm{DT50}}$. A degradation rate is calculated from the DT50 as ln(2)/DT50.

Uncertainty associated with assigning a distribution to DT50 based on a small number of measurements is included. Selection of a value for 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 DT50 is itself uncertain. Sampling uncertainty for DT50 is 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 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 DT50 is randomly sampled from that distribution.

Degradation in the case of time-dependent sorption

If the user chooses to account for an increase of sorption over time in the model (see below), degradation parameters derived from time-dependent sorption experiments must be entered in the model. A DegT50 for first-order degradation in the liquid phase and equilibrium phase is required, together with four sorption parameters. Webfram samples sets of all five model parameters from available combinations using a uniform distribution. The sampling is undertaken in the inner loop of the model. Uncertainty is not accounted for. A degradation rate is calculated as ln(2)/DegT50.

Temperature correction

In both cases, 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 simulation with MACRO 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. The Q10 value is a user input. The recommended default value for Q10 is 2.58.

$$factor = Q10^{\left(\frac{av.temp\ this\ month - 20}{10}\right)}$$

	factor
Jan	0.2852
Feb	0.2745
Mar	0.3062
Apr	0.3766
May	0.4724
Jun	0.5812
Jul	0.6394
Aug	0.5602
Sep	0.5146
Oct	0.4513
Nov	0.2912
Dec	0.2668

- 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 for a Q10 of 2.58:

Start of FC period	Application date	Time from application to start of drainflow	Correction factor	Comment
20/09/2005	01/05/2005	142	0.5536	Average May-September
20/09/2005	18/09/2005	3	0.5146	Factor for September
20/09/2005	01/10/2005	3	0.4513	Factor for October

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.

3.8 Aerial mass at time of drainflow event

In the case of instantaneous sorption, Webfram calculates the mass at the time of the drainflow event as follows:

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

with

aerial mass = aerial mass left at time of drainflow event (g/ha)

A = application rate corrected for carry over and/or interception (g/ha)

time = time between application and drainflow event (days)

k = degradation rate corrected for temperature (days^{-1})

If the user chooses to account for time-dependent sorption, the model described in Section 3.8 is used to calculate the residual mass at the time of the drainflow event.

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 (e.g. for the Denchworth soil) = 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.

3.9 Sorption

The extent of sorption in soil determines the availability of pesticide residues for transport in drainflow. The user can simulate instantaneous sorption characterised by a Freundlich isotherm or use a time-dependent sorption model.

Instantaneous sorption

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. Uncertainty associated with assigning a distribution to Koc based on a small number of measurements is included as described above for the sampling of DT50. The distributions are truncated at the 5th percentile and 95th percentile.

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 (Table 5):

Table 5. Organic carbon contents of the four soil classes included in Webfram (from SEISMIC)

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
Clifton	3.1	1.5	1.178	5.022

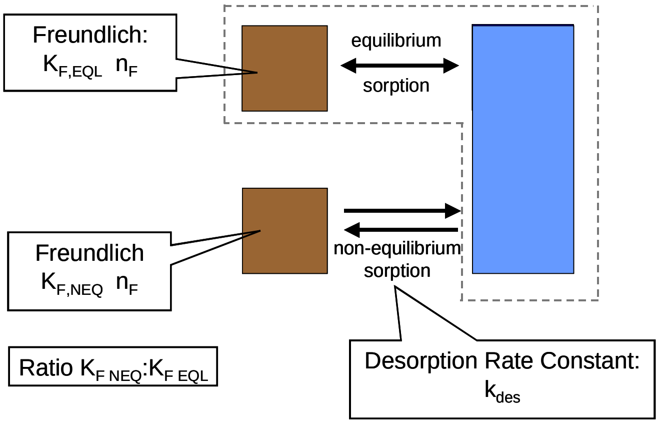
The Freundlich coefficient (Kf value) is then calculated as

$$Kf = Koc \times \% \text{ organic carbon} / 100$$

Time-dependent sorption

In reality, sorption often increases with increasing time from appplication and this reduces the availability of the pesticide in soil solution at the time of the drainflow event. Webfram users have the option to account for time-dependent sorption if experimental evidence is available. The two-site model that is implemented in the latest version of the FOCUS groundwater models PEARL (Leistra et al., 2001), PELMO and PRZM was coded in Matlab and linked with the Webfram drainage module. The two-site model is depicted in Figure 2.

Figure 2. **Schematic representation of the two-site sorption model showing the soil solution on the right and the equilibrium and non-equilibrium sorption sites on the left. Only pesticide in the equilibrium domain (indicated by the dashed line) is subject to degradation.**



The model assumes that sorption is instantaneous on one fraction of the sorption sites and slow on the remaining fraction (Leistra et al., 2001). The model does not account for irreversible sorption. Degradation is described by first-order kinetics. Only molecules present in the liquid phase or sorbed to the equilibrium sites are assumed to degrade. The model can be described as follows:

$$M_p = V\,c_L + M_s(X_{EQ} + X_{NE})$$

$$X_{EQ} = K_{F,EQ}\,c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^{n_F}$$

$$\frac{dX_{NE}}{dt} = k_d\left(K_{F,NE}\,c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^{n_F} - X_{NE}\right)$$

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

$$\frac{dM_p}{dt} = -k_t(V\,c_L + M_s\,X_{EQ})$$

k_t = ln(2)/DegT50

$K_{F,EQ} = m_{OM}\,K_{OM,EQ}$

where:

M_p = total mass of pesticide (µg)
V = the volume of water in the soil (mL)
M_s = the mass of dry soil (g)
c_L = concentration in the liquid phase (µg/mL)
$c_{L,R}$ = reference concentration in the liquid phase (µg/mL)
X_{EQ} = content sorbed at equilibrium sites (µg/g)
X_{NE} = content sorbed at non-equilibrium sites (µg/g)
$K_{F,EQ}$ = equilibrium Freundlich sorption coefficient (mL/g)

$K_{F,NE}$ = non-equilibrium Freundlich sorption coefficient (mL/g)
n_F = Freundlich exponent (-)
k_d = desorption rate coefficient (d^{-1})
f_{NE} = factor for describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients (-)
k_t = degradation rate coefficient (d^{-1})
$DegT50$ = Half-life for degradation (d^{-1})
m_{OM} = mass fraction of organic matter in the soil (kg/kg)
$K_{OM,EQ}$ = coefficient of equilibrium sorption on organic matter (mL/g)

The model has six input parameters: the initial mass of the pesticide, the degradation half-life *DegT50*, the equilibrium sorption coefficient $K_{OM,EQ}$, the Freundlich exponent n_F, the ratio of non-equilibrium sorption to equilibrium sorption f_{NE} and the desorption rate constant k_{des}. The user must enter at least four combinations of all parameters except the initial mass into Webfram. Each set must be measured within the same soil. One of the measured combinations of the five parameters is selected in each model iteration. The conversion factor between organic matter content and organic carbon of the soil is 1.724. The initial pesticide mass in soil is calculated by Webfram from the application rate, corrected for interception by the crop.

3.10 Interactions between variables

Users of Webfram have the possibility to include one of four linear relationships between key variables. These options are available in combination with instantaneous sorption:

1. logDT50 and log Koc
2. log DT50 and pH
3. log Koc and pH
4. logDT50 and log Koc as well as log Koc and pH

The user must decide whether the relationship between the measured data is strong enough to justify inclusion in the modelling. Webfram undertakes an analysis of variance and reports the p-value for the F-statistics. It is recommended that the F-test should be significant at the 5% level, *i.e.* p must be <0.05. The approach to inclusion of the four options is described below.

<u>Option 1</u>

This option enables the user to account for a dependency of pesticide degradation on the strength of sorption. The approach is summarised below:

User input	DT50, Koc
Outer loop	Bayesian regression (linear relationship between log DT50 and log Koc) Sampling of slope b and intercept a of the linear relationship between log DT50 and log Koc Sampling of parameters to calculate mean and standard deviation of normal distribution of LogKoc
Inner loop	Sampling of log Koc from the normal distribution using the mean and standard deviation from the outer loop Calculation of log DT50 = a + b log Koc using a and b from the outer loop

The user must enter measured DT50 values and Koc values into Webfram. These must be entered as pairs, each measured in the same soil. The system then tests whether a linear relationship exists between log DT50 and log Koc, (log DT50 = $a + b$ Log Koc). Webfram applies a simple linear Bayesian regression to describe the dependency. The advantage of this method over ordinary least squares regression is that it accounts for the uncertainty of the slope b and intercept a. This uncertainty arises because only a limited number of measurements is available and the data are scattered. Using the posterior distributions, Webfram predicts values for the variable on the y axis (log DT50) given the n data pairs $\{logDT50_i, logKoc_i\}$. This results in prediction intervals for the independent variable.

For each of the Monte Carlo iterations in the outer loop, a new value is sampled for the slope and intercept of the linear relationship between the two variables log DT50 and log Koc. The mean and standard deviation of the normal distribution of log Koc are also derived in the outer loop. These are based on the measurements entered by the user, taking into account the uncertainty in the distribution of log Koc due to the small number of data. In each iteration in the inner loop, a log Koc value is sampled from the normal distribution. The corresponding value of the logDT50 is calculated from the sampled log Koc value based on the linear relationship using the sampled slope and intercept.

Option 2

This option accounts for a dependency of degradation on soil pH. The user must enter measured DT50 values and the pH (H_2O) of the soil used in the laboratory degradation study. pH in water is required because this is related to the distribution of pH in the scenario soils which is also measured in water. In the event that pH in water is not available, the user would need to convert between pH in another extract (e.g. $CaCl_2$) and pH in water. The model calculates log DT50 values that are relevant for the pH range of the four soils considered within Webfram based on the relationship observed in the experiments. The mean and standard deviation of the pH values of the four soil scenarios were taken from the SEISMIC database (Table 6).

Table 6. Mean and standard deviation of the pH of the four soil classes included in Webfram (from SEISMIC)

	Mean pH	Standard deviation
Denchworth	6.3	0.9
Hanslope	7.7	0.3
Brockhurst	6.4	0.5
Clifton	5.9	0.6

Webfram samples a pH value from a normal distribution truncated at the 10th percentile and the 90th percentile in each iteration in the inner loop. The log DT50 is then calculated from the sampled pH as log DT50 = $a + b$ pH. The slope and intercept of the linear relationship between Log DT50 and pH are derived from the measurements using Bayesian regression. In each of the iterations in the outer loop, a different slope and intercept are used in order to account for the uncertainty in the linear relationship.

It should be noted that the range of pH values of the soils tested in the laboratory studies must not deviate strongly from the pH range of the four soils considered in Webfram to avoid that the calculated DT50 values are extrapolated too far beyond the measured range.

Option 3

Option 3 is identical to Option 2 except that Log DT50 is replaced by Log Koc.

Option 4

The fourth option is useful if there is a relationship between degradation and sorption and - at the same time - sorption depends on soil pH. In this case, Webfram will sample the pH from the relevant distribution for the soil class. It will then calculate log Koc from the linear relationship with pH. Thereafter, log DT50 is calculated from log Koc based on the linear regression between these two variables. Option 4 results in different log DT50 for each of the four soil classes, because the pH range differs between the soils.

3.11 Availability of the pesticide in soil water

Instantaneous sorption

In the case of instantaneous sorption, availability (%) is the mass in soil solution (mg/kg) in percent of total mass (mg/kg). This is calculated using an iterative procedure (i.e. after running the first part of the model). This is because an analytical solution does not exist.

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

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

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

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

where

θ = water content in micropores in 0-4 cm (e.g. 0.3976 L/L for Denchworth)
ρ = bulk density in 0-4 cm (e.g. 1.17 kg/L for Denchworth)
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

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

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

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

Time-dependent sorption

The model code for time-dependent sorption calculates the availability of the compound in soil solution from the simulated total mass and the liquid phase concentration at the time of the drainflow event:

$$Availability\ (\%) = \frac{100\% \times C_L \times V}{M_P}$$

where:

c_L = concentration in the liquid phase at time of drainflow event (µg/mL)

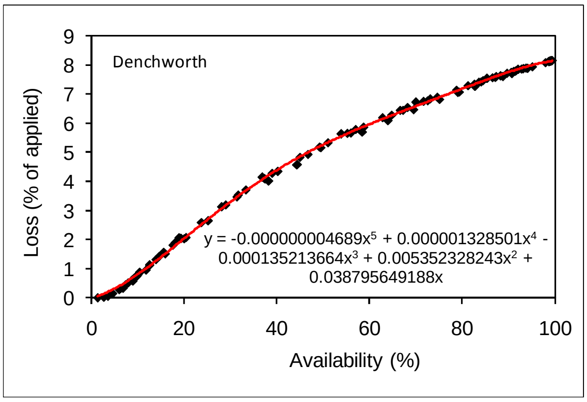
V = the volume of water in the soil at time of drainflow event (mL)

M_p = total mass of pesticide at time of drainflow event (µg)

3.12 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. This is based on calculations with the MACRO model for various combinations of pesticide properties and application rates (shown as symbols in Figure 3):

Figure 3. **Regression between % pesticide loss and % availability in solution for the Denchworth soil**



Example: availability = 9.14%, loss = 0.708%.

0.708% of 315.34 g/ha = 2.23 g/ha.

3.13 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: 2.23 g lost from a 1-ha field / 130000 L water = 1.715 x 10^{-5} g L^{-1} = 17.15 µg L^{-1}.

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