User Manual

PELMO
(Pesticide Leaching Model)

Version 5.00

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1 Introduction

This manual describes version 5.0 of the computer program PELMO which stands for "Pesticide Leaching Model". Previous versions have been developed and described by Klein (1995) and Jene (1998). PELMO is based originally on the PRZM 1 model of US-EPA (Carsel 1984), but it was independently developed since 1989.

PELMO estimates the vertical transport of pesticides in the unsaturated soil system within and below the plant root zone. The equations which describe transport and transformation of pesticides in PELMO have been selected on the basis of the test studies that are available for these substances. Information on the validation status of prior PELMO versions with lysimeter studies and groundwater monitoring are available e.g. from Hardy et al 2008, Jene et al. 1998, Jene et al. 1999, Klein et al. 1997, Trevisan et al. 2003.

PELMO considers various environmentally relevant processes. An overview on the fate processes is given in Table 1.

Table 1: Overview on processes considered in PELMO to simulate pesticide fate

Type of Process	Process	influenced by*
Fate on the crop	volatilisation	temperature
	penetration into the leaves	crop development
	photo-degradation	light intensity and crop development
	wash-off	rainfall and crop development
Distribution in the soil	Freundlich sorption	OC content and soil moisture
	moisture dependency of Sorption	soil moisture
	degradation in soil	soil depth, soil moisture and soil temperature
	hydrolysis in soil	soil pH
	volatilisation from soil surface	temperature and OC content and soil moisture
	photolysis in soil	weather, crop and soil
	degradation in soil	soil depth, soil moisture and soil temperature
	formation of metabolites	soil depth, soil moisture and soil temperature
Transport	chromatographic flow	soil properties and rainfall
	macro-pore flow	soil properties and rainfall
	via soil air	soil properties, rainfall and temperature
	run-off	rainfall, dynamic curve number
	soil erosion	rainfall, field geometry (*e.g.*, slope), run-off
	root uptake	root depth, soil water and potential evapotranspiration

* all processes are additionally influenced by compound properties

However, the model has been mainly used to estimate the leaching potential in the regulatory context mentioned above (described in more detail at e.g. FOCUS 2000, 2002, 2009, Michalski et al. 2004, website of Federal Office for Consumer Protection BVL[1]).

In chapter 2 the model algorithms are described whereas chapter 3 gives information how to run simulations and evaluate the results using the PELMO shell.

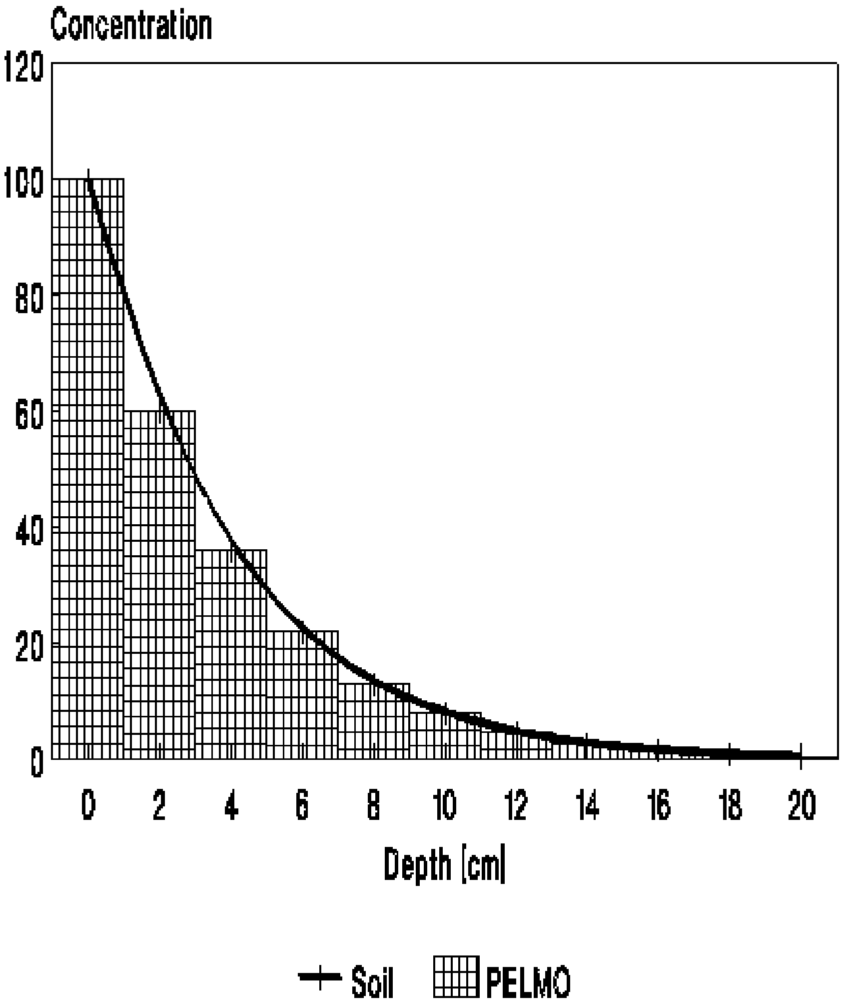

Figure 1: Concentration profile in soil reality and model representation

PELMO is a dynamic, compartmental model. The soil profile is divided into different segments (layers) from top to bottom. Within a given compartment all parameters of the simulation as soil moisture, soil density, concentration of the pesticide in soil water and soil matrix are considered being homogeneous. The thickness of these layers is usually in the range of 1 to

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[1] http://www.bvl.bund.de/DE/04_Pflanzenschutzmittel/03_Antragsteller/04_Zulassungsverfahren/07_Naturhaushalt/psm_naturhaush_node.html

5 cm. To achieve realistic soil concentrations directly at the soil surface a thin layer of 1mm is used for the top soil independent on the user input.

However, the continuous concentration profile in soil is always represented by a more or less high number of layers (see Figure 1). For each day all soil parameters are re-calculated. The soil hydrology, a key process of the program, is estimated by using a capacity model with field capacity and wilting point as most important soil parameters. Daily potential evapotranspiration (ET_{pot}) can either be a direct input parameter or estimated using the equations of Hamon. Concerning the transport of pesticides in the soil system PELMO assumes equilibrium between pesticide concentration in soil matrix, soil air and soil water after one day.

2 Model description

2.1 Temporal and spatial resolution

As shown by Vereecken et al. (2003) previous versions of PELMO did not correctly describe the soil water regime during heavy rainfalls due to the limited temporal and spatial resolution. In order to overcome this problem an additional module was implemented in PELMO 5 which uses a better temporal resolution (down to 1 hour instead of 1 day) dependent on the actual rainfall situation. The minimum and maximum time steps are defined in the range of 1 hour to 1 day (see equation 1)

$$\Delta t = Maximum\left\langle Minimum\left[\frac{\theta_{FC}\ d}{P}, 1\ day\right], 1\ hour\right\rangle \tag{1}$$

Δt Time step (d)

θ_{FC}: Soil moisture at field capacity in the first regular compartment (compartment 2)

P: Daily precipitation (cm/d)

d: Depth of the layer (cm)

2.2 Crop management

2.2.1 Crop parameters

PELMO generally considers linear growth of crops between the date of emergence (0) and the date of maturation (maximum value) independent on climate data. Between maturation and harvest the maximum values for the LAI and the active crop rooting depth are considered. However, there are two exceptions, the first with respect to the parameter *maximum rooting depth*": if a crop is marked as "perennial" the maximum rooting depth will be considered directly after crop emergence and stays at this value until harvest. The other exception is the implementation of the new parameter "spring point". If the "spring point" is set there will be a hibernation period between emergence and the spring point where the crop only slowly grows. The parameter was introduced to improve the modelling of crops which are planted in autumn but which do not grow significantly before spring. The "spring point" is a crop specific parameter which is saved in the scenario file.

Linear growth refers to the parameters *root depth*, *interception storage for water*, *dry mass*, and *maximum leaf area index (LAI)*. If a spring point is defined *root depth, interception storage* *for water* and *dry mass* reach 10% of the maximum value at this time. The parameter *LAI* at spring point is set to 0.1 independent on the crop.

The LAI is a new parameter of PELMO 5.0 which is used to calculate dynamic crop and water interception values. Reinken et al. (2013) identified significant differences between PEARL and PELMO with respect to the parameterisation of wash-off calculations. These differences were primarily caused by differences in the calculation of the fraction of the surface area of the soil covered by the crop, i.e. SC (EFSA 2017). It is assumed that the fraction of the dose intercepted by the crop equals SC. The description of crop development was therefore harmonised. It is now assumed that the LAI increases linearly between emergence date and the date at which the maximum LAI occurs. Furthermore, it was decided to base the soil cover needed in the wash-off calculations on Beer's law according to following equation:

$$\mathrm{SC} = 100\ \left[1 - \exp(-\mathrm{e} \cdot \mathrm{LAI})\right] \qquad (2)$$

SC *crop interception factor* [%]

e: *Beer's law extinction coefficient* (set to 0.39)

LAI: leaf area index (m^2/m^2)

In the following two figures crop development is presented for standard annual crops and for crops where a spring point was defined.

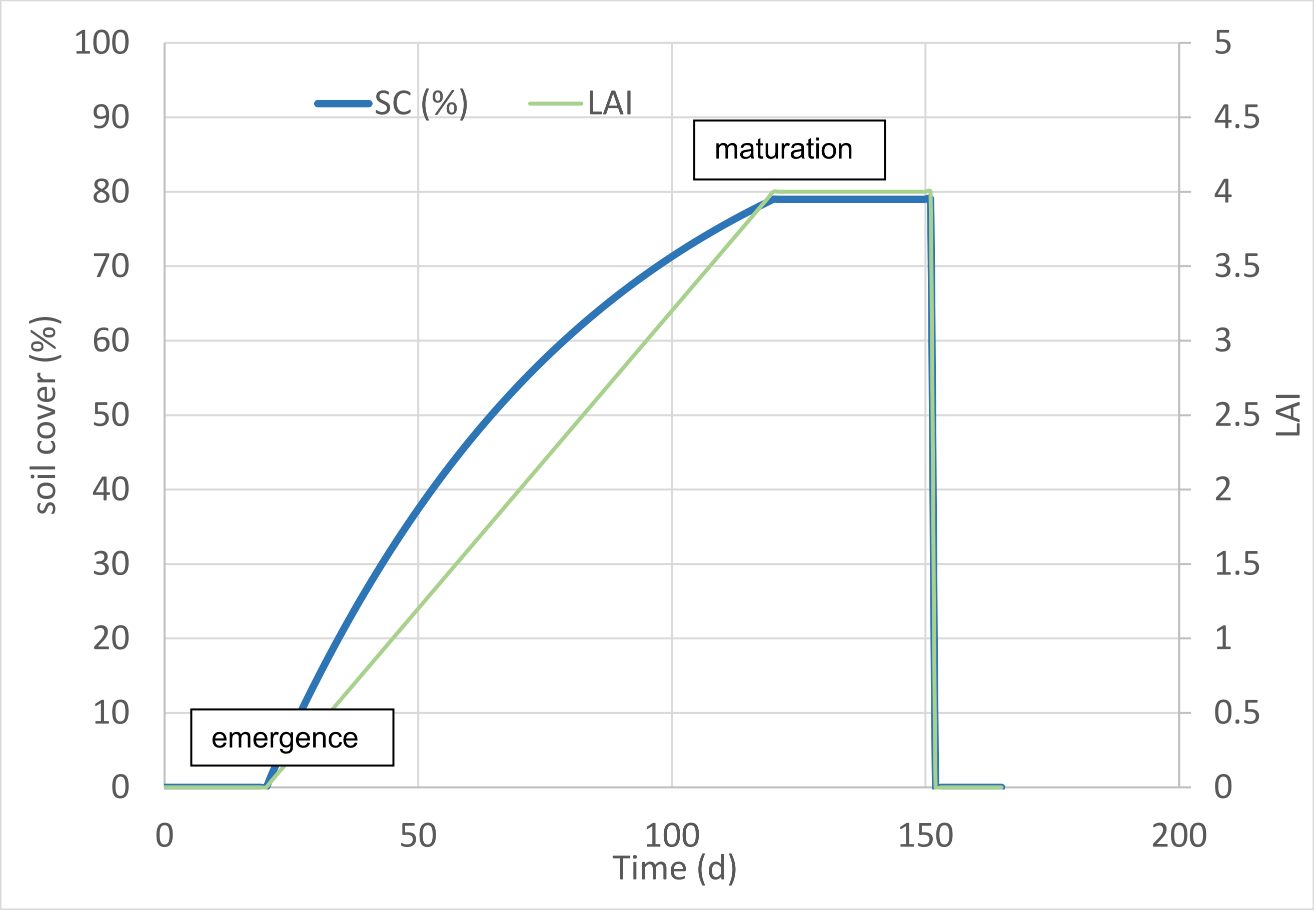


Figure 2: Crop development between emergence and harvest for standard annual crops

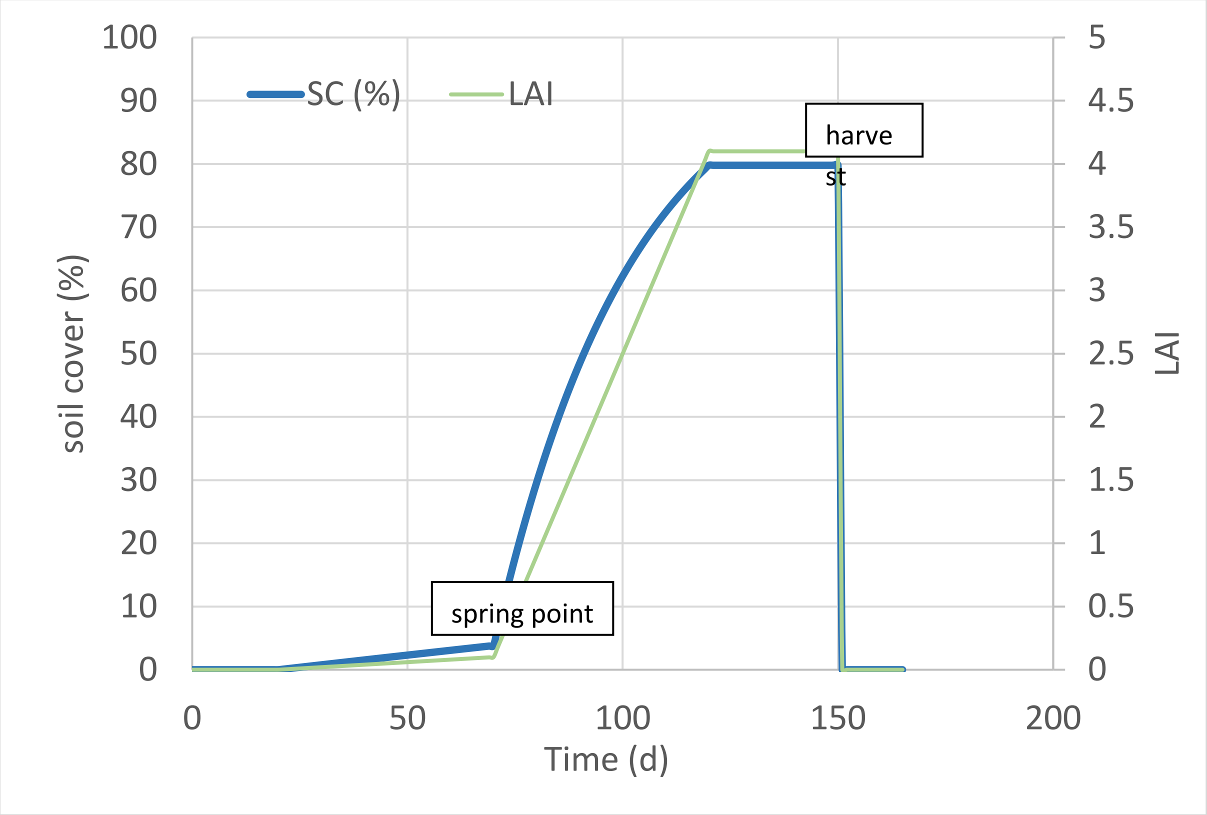


Figure 3: Crop development between emergence and harvest for winter crops

Furthermore, for spray applications onto crops without leaves (during autumn and winter) a special procedure was developed because the LAI is zero or very low and PEARL and PELMO would simulate no water or substance would be washed-off of water from plant surfaces. This was solved based on specifying a minimum LAI that corresponds to the respective crop interception.

The values for the parameters *LAImin* and *LAImax* can be entered in the scenario file. Based on the dynamic LAI daily soil cover is calculated. The actual rooting depth is used to calculate to which depth soil water is extracted by the crop.

If the user chooses to let PELMO estimate the distribution between plants and the soil by an exponential function additionally the maximum foliar dry mass has to be specified. The actual foliar dry mass at the time of application is then calculated similarly as the other crop parameters based on the emergence and maturation day.

Finally, specific crop parameters have to be selected or individually defined, when run-off after heavy rainfall events should be considered as an additional process. The interaction between soil type, land use and crop cover is accounted for by assigning a run-off curve number (RCN) for average soil moisture conditions to important soil cover complexes for the fallow, cropping and residues parts of a growing season. PELMO will then calculate the actual RCN dependent on the crop growth and the soil moisture in the top soil.

2.2.2 Crop rotation

PELMO considers crop rotation. In order to define the crop rotation either generalised predefined cropping information about tillage, emergence, maturation, senescence, harvest must be selected or specific information must be provided by the user.

The crop rotation influences the depth to which water is extracted by plants (crop dependent). When doing standard FOCUS simulations crop rotation may be simulated by growing the same crop in each year of the simulation period but with applications only every second or third year mimicking crop without applications of the test substance in a rotation in years without growing the treated crop.

2.2.3 Tillage

PELMO is able to simulate tillage before sowing the crop. Tillage will lead to a mixing of the substance from the soil surface up to the tillage depth and is always related to a crop.

If tillage should be considered in a simulation the tillage date must be given (which has to be before crop emergence). Then, the tillage depth has to be specified, which is independent on the crop, but constant for a simulation. Notice, that tillage is not a crop parameter in PELMO. Instead tillage is considered always for the whole simulation including all crops planted. The tillage depth and the tillage dates are saved in the scenario file.

2.3 Soil water regime

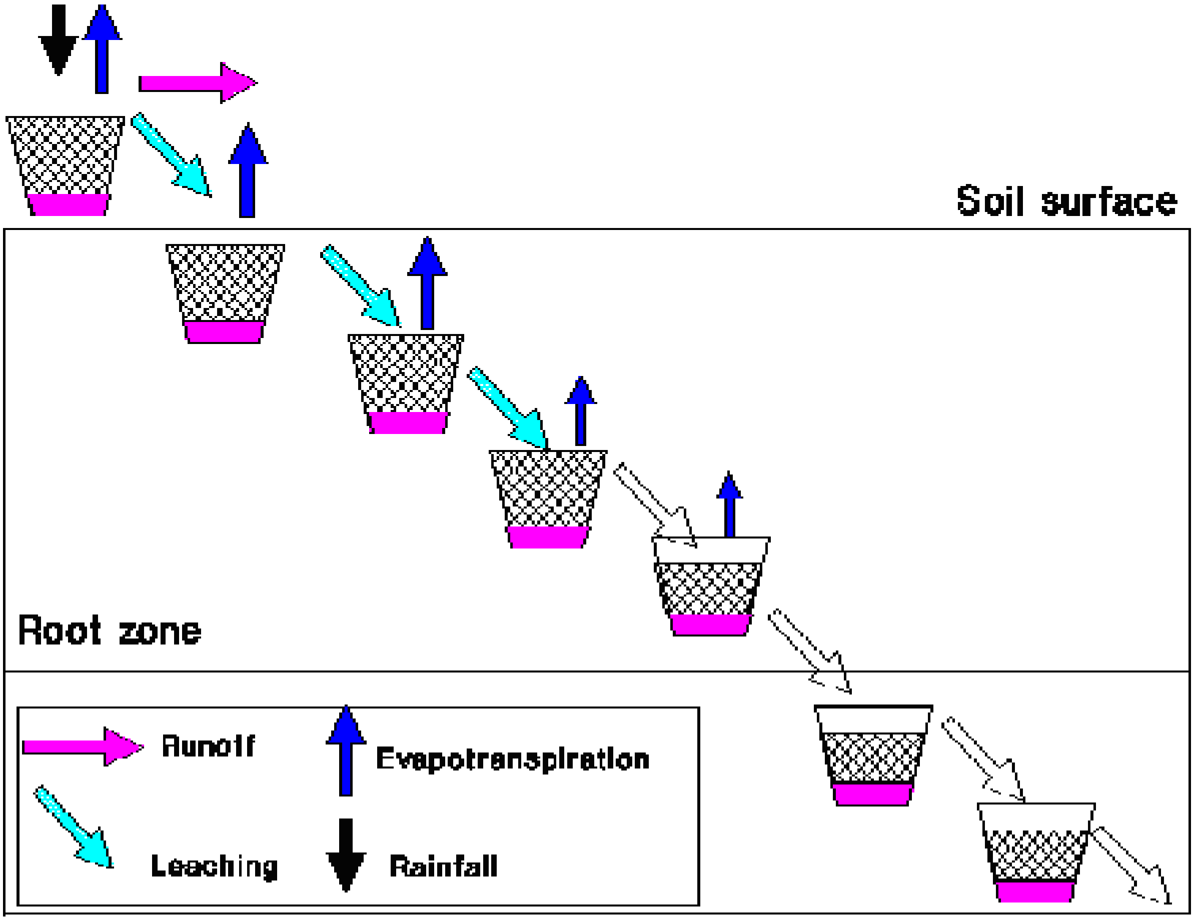


Figure 4: Schematic representation of PELMO's soil water regime

To calculate the soil water regime PELMO uses the field capacity approach (Carsel et al. 1984). The soil is divided into different layers. All parameters (e.g. soil density, soil moisture, temperature, but also the concentration of the pesticide) are considered being homogeneously distributed within these compartments. To adequately describe the gradients of concentrations in soil an adequate number of segments is necessary and the layer thickness should be kept in a limited range (e.g. $\leq$ 5 cm).

Dependent on the soil depth different processes determining the water content are considered. The model distinguishes between the surface layer, the segments in the root zone, and the compartments below the root zone.

Daily updating of soil moisture in the soil profile requires additional calculations for evapotranspiration (see chapter 2.3.2), irrigation (see chapter 2.3.3), run-off (see chapter 2.3.5), snow melt (see chapter 2.3.7) and percolation (see chapter 2.3.8).

Incoming precipitation and irrigation is first partitioned between snow and rain depending upon temperature. Air temperatures below 0 °C produce snow. Precipitation and/or irrigation first encounters plant interception and the remaining daily volume is available for the run-off equation (see section 2.3.5).

The calculation of percolation is rather simplistic using the assumption that seepage only occurs if the soil moisture is above field capacity. Capillary rise from deeper soil layers is generally not simulated.

2.3.1 Potential Evapotranspiration

The estimation of evapotranspiration (which is defined in PELMO as the sum of evaporation and transpiration) is an important process for the description of soil hydrology. An adequate description of this process is therefore the bases for an adequate description of the water and pesticide transport in soil.

Already PRZM-1 had different options to estimate the potential evapotranspiration depending on the availability of input data. In PELMO the number of options has been increased to the following options:

- no calculation of potential evapotranspiration, the user will directly enter daily data on potential evapotranspiration,
- calculation of potential evapotranspiration according to the Hamon-equation.

2.3.1.1 Calculation of potential evapotranspiration according to Hamon

PELMO was developed on the basis of the PRZM-1 model. It is therefore possible to estimate the potential evapotranspiration based on the equations implemented in PRZM-1. PRZM-1 will use the equation of Hamon if no data on potential evapotranspiration is available. For the calculation the average air temperature and the light day hours are necessary according to following equation:

$$Epot = \frac{0.021 \cdot ES(Temp)\, n_h^2}{Temp} \qquad (3)$$

n_h: *Number of light day hours per day (h)*

ES: *Saturated vapour density [Torr]*

$Temp$: *average daily air temperature [°C]*

The daylight hours which are used for the estimate are automatically calculated based on the latitude of the location and the season considering the following table:

Table 2: Maximum length of daylight hours and amplitude versus latitude of the location

Latitude	0.00	16.44	30.48	41.24	49.03	54.31	58.27	63.23	66.50
LDH_{max} *[h]*	12	13	14	15	16	17	18	20	24
A_{max} *[h]*	0	1	2	3	4	5	6	8	12

Source: Diercke Weltatlas, Georg Westermann Verlag, Braunschweig 1974

The daylight hours will be calculated for every day of the year according to the following equation.

$$n_h = 12 + A_{max} \sin\left[(J_{Day} - 80) * 2\pi / 365.0\right] * \mathrm{sign}(Lat) \qquad (4)$$

n_h: day light hours [h]

A_{max}: Maximum deviation of current light day hours from the standard (12 h) [h]

J_{Day}: Day counter (Julian day: 0 to 365)

Lat: Latitude [°]

The number 80 has to be subtracted from the Julian day of the year because otherwise the situation of March 21 (no deviation from standard day length of 12 hours) will occur already on January 1. Locations which have negative latitudes will be calculated with opposite signs (signum-function). Monthly averaged numbers for the daylight hours will be used for the simulation which will be calculated once at the beginning of the simulation.

2.3.1.2 Direct input of potential evapotranspiration

Daily evapotranspiration data can be directly entered as part of the climatic data files together with rainfall and temperature data always required for degradation processes. Potential evaporation is usually related to a standard coverage. It is therefore possible to linearly correct this standard information dependent on the crop used in the simulation. In the previous versions of the model correction was done based on a single Kc-factor which was used throughout the whole period of the simulation. In the new version of PELMO the module was extended to consider time varying crop Kc factors. The extension was done as a result of the recommendation of the FOCUS groundwater group in order to harmonise the results of the European leaching models. As described in FOCUS (2009) a common procedure was recommended in which the year was divided into the following four periods

- Harvest to emergence (period 1)
- Emergence to maximum LAI (period 2)
- Maximum LAI to senescence (period 3)
- Senescence to harvest (period 4)

Constant *Kc factors* are assumed for each period. As a consequence *Kc-factors* must be defined for following crop stages:

- no crop (*Kc0*,
- mid season (*Kc1*),
- late season (*Kc2*).

The respective *Kc*-factors for the 4 periods are calculated as follows:

Period 1: $Kc = Kc0$ (5)
Period 2: $Kc = (Kc0 + Kc1)/2$ (6)
Period 3: $Kc = Kc1$ (7)
Period 4: $Kc = (Kc1+Kc2)/2$ (8)

2.3.2 Actual evapotranspiration

Similar as in PRZM the daily evapotranspiration is divided into evaporation from canopy, soil evaporation and crop transpiration. Total demand is first estimated and then extracted sequentially from crop canopy storage and from each layer until wilting point is reached in each layer or until total demand is reached. Evaporation occurs down to a user specified depth. The remaining demand - crop transpiration – is taken from the layers between this depth and the active rooting depth.

A triangular root distribution is assumed from the surface zone to the maximum depth of rooting with the maximum root density assumed to be near the surface. Actual evapotranspiration is also limited by soil moisture availability. If the soil moisture is below wilting point no soil water will be extracted. The water extracted by transpiration is proportional to the root density in the respective layer.

$$\mathrm{ET_i} = \mathrm{Minimum}\left\langle \left(\mathrm{SW_i} - \mathrm{WP_i}\right) \cdot \mathrm{fd_i}, \mathrm{ET_p} - \sum_{k}^{k-1} \mathrm{ET_k} \right\rangle \qquad (9)$$

ET_i: actual evapotranspiration from layer i

SW_i: soil water content in layer i (cm³/cm³)

WP_i: wilting point water content of layer i (cm³/cm³)

fd_i: depth factor for layer i

The depth factor *fd* is internally set in the code. It linearly weights the extraction of water from the root zone with deph in a triangular fashion with the maximum root density at the soil surface.

2.3.3 Irrigation

It is possible to simulate automatic irrigation generated by the model dependent on the crop type. Irrigation schedules are provided from the time of planting until start of senescence and are generated using an irrigation routine, which applies irrigation once a week on a fixed day to bring the root zone up to field capacity. The day cannot be changed by the user. However, irrigation will be applied only if the amount required exceeded 15 mm in the active rooting depth.

$$\mathrm{IRR} = \sum_{i=1}^{nroot} \left(\mathrm{SW_i} - \mathrm{FC_i}\right) \mathrm{depth_i} \qquad (10)$$

IRR: irrigation added to the rainfall (cm)

SW_i: soil water content in layer i (cm³/cm³)

FC_i: field capacity water content of layer i (cm³/cm³)

$depth_{ii}$ depth of the soil layer i

nroot: dynamic number of soil layers with active roots

In the current FOCUS groundwater scenarios sprinkler irrigation was considered for all crops. Irrigation is simply added to the rainfall and can be intercepted by the canopy like rainfall. According to EFSA soil guidance drip irrigation to the soil surface may be more appropriate for permanent crops. However, drip irrigation was not an option in previous PELMO versions. In the new version an option for drip irrigation was implemented in PELMO. If drip irrigation is selected the additional water is added to the soil surface below the canopy. Further irrigation regimes such as local spot application are not considered

2.3.4 Wash-off

Already in previous versions of PELMO crop canopy processes and foliar wash-off could be simulated. However, Reinken et al. (2013) identified serious differences between PEARL and PELMO with respect to the parameterisation of wash-off calculations.

The EFSA working group concluded that these differences were primarily caused by differences in the consideration of the crop cover and development. Crop development was harmonised by implementing a spring point for winter crops into PELMO (see section 2.2.1 in this document). Additionally, the calculation of wash-off amounts in PELMO was modified in order to consider the actual crop cover fraction for the amount of rainfall that is considered for the wash-off from the plant canopy (see the following equation; note that in previous versions of PELMO simply the whole rainfall was considered for wash-off independent on the actual crop cover):

$$W = P \frac{SC}{100} \tag{11}$$

W Wash-off intensity [mm/d]

P: Daily precipitation [mm/d]

SC crop interception factor [%]

2.3.5 Run-off

PELMO is simulating run-off according to the Run-off Curve Number approach according to following equation.

$$Q = \frac{(P - 10\,S)^2}{(P + 40\,S)} \qquad (12)$$

$$S = 0.508\ L/m^2\ (1000\ RCN^{-1}\ -10) \qquad (13)$$

S:	retention parameter (L/m²)
Q:	Run-off [L/m²]
RCN:	dynamic Run-off-Curve Number
P:	Precipitation [L/m²]

Specific curve numbers are calculated for each day internally.

The daily RCN calculated from PELMO is dependent on the surface condition (fallow, residue, type of crop) and on the soil moisture conditions in the top 10 cm. If the soil moisture is exactly between field capacity and wilting point the “standard” numbers given in the table below are used. For wetter soils corrections of the standard RCN are made in direction of higher values, for dryer soil respective lower values are considered.

PELMO uses predefined crop dependent run-off curve numbers as summarised in Table 3.

Table 3: Predefined RC-Numbers for different crops and hydrologic soil groups

SCS soil group:	A	B	C	D
- fallow + residue	77	86	91	94
– apples (orchards)	36	60	73	79
– grass (+alfalfa)	30	58	71	78
– potatoes	62	83	89	93
– sugar beet	58	72	81	85
– winter cereals	54	70	80	85
- beans (field+vegetable)	67	78	85	89
– bush berries	36	60	73	79
– cabbage	58	72	81	85
– carrots	58	72	81	85
– citrus	36	60	73	79
– cotton	67	78	85	89
– linseed	54	70	80	85
– maize	62	83	89	93
– oil seed rape (sum)	54	70	80	85
– oil seed rape (win)	54	70	80	85
– onions	58	72	81	85
– peas (animals)	67	78	85	89

The four hydrologic soil groups mentioned in Table 3 are defined as:

A. deep sand, deep loess, aggregated silts, minimum infiltration of 0.76-1.14 cm/h
B. shallow loess, sandy loam, minimum infiltration 0.38 – 0.76 cm/h
C. clay loams, shallow sandy loam, soils low in org. content, and soils usually high in clay, minimum infiltration 0.13 – 0.38 cm/h
D. soils that swell significantly when wet, heavy plastic clays, and certain saline soils, minimum infiltration 0.03 – 0.13 cm/h

Run-off influences the leaching calculations as it prevents water from percolating into deeper soil layers. As a worst case assumption run-off is switched off for FOCUS Tier 1 calculations

.

As mentioned earlier the new PELMO version is able to simulate irrigation (see chapter 2.3.3). The internal routine is constructed in a way that it does not lead to runoff. However, if irrigation is manually added to the precipitation it can lead to runoff

2.3.6 Soil erosion

The soil loss is estimated based on the amount of run-off according to the *Modified Universal Soil loss Equation* (MUSLE), as developed by Williams (Williams 1977).

$$X = a\,(V_R\,Q_P)^{0.56} * K * L_S * C * P \tag{14}$$

X: soil loss [tons]
a: conversion factor
V_R: volume run-off [m^3]
Q_P: intensity of the surface run-off [m^3 d^{-1}]
K: soil-erodibility-factor
L_S: length slope-factor
P: supporting practice factor
C: soil cover factor

In FOCUS tier 1 simulations soil erosion is not considered as the volume of run-off water is always 0. Default values for the MUSLE parameters are not available

2.3.7 Snow melt

Snow melt is estimated on days in which a snow pack exists and temperatures are above freezing point according to following equation:

$$M_{snow} = f_{snow} \cdot Temp \qquad (If\ Temp > 0\,°C) \tag{15}$$

M_{snow}: snow melt (cm)
f_{snow}: degree day snow melt factor (cm °C^{-1} day^{-1})
$Temp$: current daily average soil temperature (°C)

The default value in PELMO for the snow melt factor is 0.46 cm °C^{-1} day^{-1}

2.3.8 Soil water flow

2.3.8.1 Chromatographic flow

For the calculation of the daily amount of percolation in the soil matrix two simple drainage options (free and restricted) are available.

If the soil water is calculated to be in excess of field capacity *"free drainage"* means that the excess water above field capacity will drain to the next soil compartment within one day. The consequence of that strict rule is that soil compartments below the active root zone quickly reach field capacity and remain at that value until the end of the simulation period. This is because upward flow due to capillary rise is not simulated and plant roots are not available at these depths.

The other option "restricted drainage" was implemented for soils having layers of lower permeability that restrict the fast drainage. When using this option PELMO will calculate soil moisture above field capacity for periods of time. Instead it will drain following an exponential equation until field capacity is reached. For the calculation an additional parameter is needed the drainage rate ($k_{drainage}$) as shown in the following equation. If drainage is fast or slow depends on the drainage exponent $k_{drainage}$.. Restricted drainage is generally not used for FOCUS simulations.

:

$$\Theta_i^{t+1} = (\Theta_i^{t*} - \Theta_{FCi}) \cdot e^{-k_{drainage}\Delta t} + \Theta_{FCi} \tag{16}$$

Θ_i^{t+1}: soil moisture in compartment i at time step $t+1$ (m^3/m^3)

Θ_i^{t*}: soil moisture in compartment i at time step t including current percolation from the the next layer above (m^3/m^3)

Θ_{FCi}: soil moisture at field capacity in compartment i (m^3/m^3)

$k_{drainage}$: drainage parameter (day^{-1})

Δt: time step (day)

Field capacity (maximum soil moisture) and wilting point (minimum soil moisture) are key parameters for the soil water flow. These parameters can be entered either directly or calculated with a pedotransfer function based on other easily measurable soil parameters. Two equations are available for the estimation of field capacity and wilting point:

1) Regression based on soil density, org. carbon content, sand and clay content (taken from PRZM 1, see Carsel et al 1984),

2) PTF of PELMO (This equation was tested within the scope of the validation study with lysimeter experiments. (Klein et al. 1997)):

$$FC = (f_{clay}*60 + f_{sand}*20 + f_{silt}*40) / 100 \qquad (17)$$

$$WP = (f_{clay}*40 + f_{sand}*3 + silt* 7) / 100 \text{ (clay content above 50 \%)} \qquad (18)$$

$$WP = (f_{clay}*30 + f_{sand}*3 + f_{silt}* 7) / 100 \text{ (clay content below 50 \%)} \qquad (19)$$

WP: wilting point [Vol %]

FC: field capacity [Vol%]

f_{Clay}: clay fraction [-]

f_{Silt}: silt fraction [-]

f_{Sand}: sand fraction [-]

2.3.8.2 Macropore flow

PELMO is based on a simplified description for the movement of water in soil. Consequently also a simple functional approach has been adopted that fits to the calculation of the current chromatographic flow domain.

Water flow in macropores is not explicitly modelled. Instead, water moving in macropores is assumed to be taken up into the matrix at a user-defined depth corresponding to the base of the macropores. A two-parameter linear response model with a threshold as shown in the following equation is assumed which requires four additional parameters. The threshold is compared with the daily inffiltration which is calculated by the water reaching the soil including irrigation and snowmelt but without run-off.

$$\begin{aligned} &I_{ma} = 0, \quad I_{mi} = R \quad ; \quad I \le I_c \\ &I_{ma} = f\left(I - I_c\right), \quad I_{mi} = \left(1 - f\right)\left(I - I_c\right) + I_c \quad ; \quad I > I_c \end{aligned} \tag{20}$$

I_{ma}: amount of water routed into macropore (cm)

I_{mi}: amount of water routed into soil matrix (cm)

I_C: threshold daily infiltration which generates infiltration into macropores (cm)

I: daily infiltration (cm)

f: fraction of the excess rainfall which is routed into macropores (-)

2.3.8.3 Soil moisture at the soil surface

In the surface layer soil moisture is calculated based on a couple of processes as described in the following equation:

$$SW_0^{t+1} = SW_0^t + P_{CI} - ET_0 - L_0 - R_0 - I_{ma1} + SM \tag{21}$$

SW_0^{t+1}: soil water in the first soil layer at time step $t+1$ (*cm*)

SW_0^t: soil water in the first soil layer at time step t (*cm*)

P_{CI}: net precipitation reaching the soil surface (*cm*)

ET_0: Evapotranspiration out of the surface layer (*cm*)

I_{ma1}: amount of water routed into macropore out of the surface layer (*cm*)

L_0: Leaching to deeper soil layers (*cm*)

R_0: Run-off out of the surface layer (*cm*)

SM: Snow melt (cm)

This layer has a width of 1 mm which cannot be changed by the user.

Due to the extreme temperature fluctuations the soil surface may dry out even below wilting point up to air dried soil moisture conditions especially on days without rainfall and snow melt. The relationship in the following equation is used (Scheffer et al. 1989) to correct for this process. The influence on soil water regime and on pesticide leaching is very limited, but it may influence the volatilisation of pesticide.

$$RH = e^{\frac{M_W \cdot a \cdot H_W}{R\,T}} \qquad H_w = \frac{\ln(RH)\,R\,T}{M_w\,a} \qquad (22)$$

$$H_W = \frac{10^{pF}}{100} \qquad pF = 2 + \log(H_w) \qquad (23)$$

RH relative humidity in air (-)

M_W: molecular mass of water (18 g/mol)

a: acceleration of gravity (9.81 m/s²)

H_W: Hydraulic head (m)

R: gas constant (8.414 J K^{-1} mol^{-1})

T: Temperature (K)

pF: soil pF value

Based on equation above the pF-value is calculated using the relative humidity in air. The actual soil moisture at the soil surface is then calculated assuming equilibrium conditions between relative humidity and soil moisture at the soil surface. If the soil moisture calculated in (18) is different from (17) the moisture content in the following soil layer (the first real soil layer) is corrected to account for the correct mass balance in the system.

2.3.8.4 Soil moisture in first soil layer

Below the surface layer the first soil layer is located. The calculation is performed similarly as in the first surface layer as shown in the following equation. In contrast to the surface layer precipitation and snow melt are not considered. The amount of runoff and macropore flow is distributed between surface layer and first soil layer considering their thicknesses as weighting factor.

$$\mathrm{SW}_1^{t+1} = \mathrm{SW}_1^{t} - \mathrm{R}_1 - \mathrm{ET}_1 - \mathrm{L}_1 + \mathrm{L}_0 - \mathrm{I}_{ma1} \tag{24}$$

SW_1^{t+1}: soil water in the first soil layer at time step $t+1$ (cm)

SW_1^{t}: soil water in the first soil layer at time step t (cm)

P_{CI}: net precipitation reaching the soil surface (cm)

R_1: Run-off out of the first soil layer (cm)

I_{ma1}: amount of water routed into macropore out of the first soil layer (cm)

ET_1: Evapotranspiration out of the surface layer (cm)

L_1: Leaching to deeper soil layers (cm)

L_0: Leaching from the soil surface (cm)

R_1: Run-off out of the first soil layer (cm)

The soil water is simply converted into the soil moisture considering the depth of the respective soil layer according to following equation:

$$\Theta = \frac{SW}{d} \tag{25}$$

Θ : volumetric soil moisture in the soil layer (m^3/m^3)

SW: soil water in the soil layer (cm)

d: depth of the soil layer (cm)

2.3.8.5 Soil moisture in following soil layers

The calculation of soil moisture below the first soil layer is principally similar. However, runoff is not occurring in these layers as shown in the following equation.

$$SW_i^{t+1} = SW_i^t - ET_i - L_i + L_{i-1} \qquad (26)$$

SW_i^{t+1}: soil water in soil layer i at time step $t+1$ (cm)

SW_i^t: soil water in soil layer i at time step t (cm)

ET_i: Evapotranspiration out of soil layer i (cm)

L_i: Leaching from soil layer i to deeper soil layers (cm)

L_{i-1}: Leaching from soil layer $i+1$ into soil layer I (cm)

R: Run-off out of the surface layer (cm)

2.4 Soil temperature

Degradation processes in soil are usually strongly dependent on temperature. Therefore it is important to consider the seasonal fluctuations of soil temperature at different soil depths when estimating pesticide leaching with computer models. However, it is not necessary for the user to enter all requested soil temperatures. Instead he can request on empirical functions implemented in PELMO estimating daily soil temperatures and the daily amplitude of temperature in soil depending on soil depth on the basis of average air temperatures. The functions are based on experimental soil and air temperatures of two locations (Schmallenberg and Monheim) at 10, 30, 60 and 90 cm depth (Schäfer 1991)

$$T = T_{previous\ day} + \Delta t * (T_{air} - T_{previous\ day}) * 0.346 * \exp(-0.027028\ cm^{-1} * d) \quad (27)$$

T:	soil temperature (°C)
$T_{previous\ day}$:	soil temperature of the previous day (°C)
T_{air}:	air temperature (°C)
d:	minimum soil depth of the soil layer (cm)
Δt:	time step (d)

The equation uses the soil temperature of the previous day to estimate the soil temperature of the current day. If there is a deviation between the soil temperature of the previous day and the air temperature of the current day a correction will be made in direction of the current air temperature. The extent of the correction depends on the soil depth (with increasing soil depth, the correction decreases).

The initial soil temperature of all soil compartments will be derived within an initial run based on the temperatures of the first year.

$$A = 0.149558 + A_0 * 1.173767 * \exp(-0.099\ cm^{-1} * d) \quad (28)$$

A:	intra day soil temperature fluctuation at depth d (°C)
A_0:	air temperature fluctuation (Tmax –Tmin, °C)
d:	soil depth (cm)

The intra-day fluctuations in the previous equation are not calculated if hourly meteorological data are provided in the meteorological file.

2.5 Pesticide fate

PELMO considers different processes for the plant canopy, the surface and subsurface zones which are described in the following chapter in more detail.

2.5.1 Application

PELMO considers following types of pesticide application

- application to bare soil,

- incorporation of pesticide down to a user defined depth,
- application to the crop canopy and crop interception defined by the user,
- application to the crop canopy and crop interception calculated by the model.

If the third or fourth option is selected the actual application rate which reaches the soil surface at the day of application App_{act} will be calculated based on the nominal application rate and the actual crop interception factor using the following equation.

$$\mathrm{App}_{\mathrm{act}} = \mathrm{App}_{\mathrm{nom}} \cdot \frac{100 - \mathrm{SC}}{100} \tag{29}$$

App_{act}: actual application rate applied to the soil surface [kg/ha]

App_{nom} nominal application rate to the plant/soil system [kg/ha]

SC crop interception factor [%], see equation (2)

If the user did not enter the crop interception factor manually calculated crop interceptions are based on dynamic interception percentages correlated with the development of the crop assuming linear growth from emergence to maturation.

It is furthermore possible to define two deposit classes: a well-exposed and a poorly-exposed class which will influence the results of the fate modelling on plant surfaces. This feature is not designed for standard FOCUS simulations as it only works when simulations are started from the user specific part of the shell. The deposit in the latter class may be enclosed by plant parts (e.g. in leaf axils), it might be located on the lee side of the air flow, or it is assumed that they are located deeper in the canopy. It does however not influence the crop interception and the fraction which is reaching soil at the day of applications. The deposit class influence the degradation and volatilisation of pesticide from the canopy.

More information on deposit classes is given in chapter 2.5.3 (Plant surface).

2.5.2 Rapidly dissipating fraction derived from field dissipation studies

EFSA provided guidance for the calculation of the rapidly dissipating fraction at the soil surface (Ffield) from field dissipation studies. The correction based on Ffield should apply to only the fraction of the dose that directly reaches the soil surface since it is unlikely that fast dissipation processes play an important role for the fraction that is washed off from the canopy. Significant wash-off will only occur if the crop has covered the soil to a large extent and fast dissipation processes at the soil surface are likely to be less significant when the soil is covered to a large extent.

According to the EFSA (2015) DegT50 guidance Ffield has to be specified for each application of the substance. Ffield was implemented in the new versions of PELMO and PEARL as an additional input parameter and it is used to calculate the actual application dose (A_{act}) that reaches the soil surface on the day of application (the part that penetrates immediately into the soil matrix). In the following equation F_{field} is the rapidly dissipating fraction, f_{soil} the fraction that reaches the soil surface when considering crop interception, and A the nominal dose.

$$App_{act} = f_{soil} \left(1 - F_{field}\right) App \qquad (30)$$

A_{act}: actual dose that reaches the soil and is left after fast disappearance processes that undergoe regular soil degradation (kg/ha)

F_{field}: rapidly dissipating fraction (-)

f_{soil}: fraction that reaches the soil surface when considering crop interception (-)

A: nominal dose (kg/ha)

2.5.3 Plant surface

In order to improve the fate of pesticides on plants new models were implemented into PELMO 5 which simulates the environmental fate of pesticides on an hourly basis after application, including volatilisation from leaves, penetration into leaves, wash-off and photo-transformation. There is no sequence processes are occurring in parallel with a short time step of 1 hour. All canopy processes are calculated based on the same amount (at the beginning of the day). In order to prevent negative amounts on the canopy and to mimic exponential behaviour additional internal loops were implemented which calculates the fluxes based on 1/40 of the actual time step. The model algorithms were validated with experimental data sets (Wolters et al. 2004, Wolters et al. 2004).

Wash-off

The amount of pesticide washed off from the leaves by rainfall is set dependent on wash-off intensity and a wash-off coefficient. If hourly rainfall data is not given daily data is transferred to hourly values by dividing by 24. If - according to the equation - the calculated amount of pesticide washed-off exceeds the amount on the canopy then the amount washed off is set to the total amount.

$$R_w = k_w W_r A_p \tag{31}$$

R_w	amount of pesticide wash-off from the leaves [kg/(m^2 d)]
k_w	coefficient for pesticide wash-off [1/cm]
W	Wash-off intensity [cm/d]
A_p	areic mass of pesticide on the plants (kg/m²)

Penetration

The amount of pesticide penetration into the leaves is calculated by:

$$R_{pen} = k_{pen} A_p \tag{32}$$

R_{pen}	amount of pesticide penetration into the leaves [kg/(m^2 d)]
k_{pen}	rate coefficient of penetration [1/d]

If, according to the equation, the calculated amount of pesticide penetrated into the leaves exceeds the amount on the leaves then the amount penetrated is set to the total amount on the surface.

If the fate on plant surfaces should be calculated without separation of photo-degradation, penetration and volatilisation (lumped disappearance rate) the penetration should be used.

Volatilisation

Volatilisation of pesticide from the leaf surface is determined by vapour diffusion through the laminar air boundary layer. The potential rate of volatilisation of pesticide from the deposit/leaf surface is calculated by:

$$J_{vol,pot} = D_{air} \frac{\left(C_{a,s} - C_{a,t}\right)}{d_{lam}} \tag{33}$$

$J_{vol,pot}$ potential flux of volatilisation from the surface [kg/(m^2 d)]

$C_{a,t}$ concentration in the turbulent air just outside the laminar air layer,kg/m^3 (set at zero)

$C_{a,s}$ vapour concentration at the leaf surface (kg/m^3)

d_{lam} equivalent thickness of the laminar air boundary layer (m)

D_{air} diffusion coefficient of pesticide in air, m^2/d

The vapour pressure at the deposit/leaf surface is assumed to be saturated, dependent on the temperature. It is assumed that the increase of the vapour pressure is constant for a given temperature increase (e.g. 10 °C). It is recommended to consider a factor of 4 for an increase of 10 °C if the vapour pressure is not known at different temperatures.

The coefficient for diffusion of the pesticide in air at the reference temperature is estimated according to the following equation:

$$D_{air} = D_{air,ref} \left(\frac{T}{T_{ref}} \right)^{1.75} \tag{34}$$

$D_{air,ref}$ diffusion coefficient in air at reference temperature, m^2/d

The actual amount of pesticide volatilisation is described by taking into account the mass on the plants:

$$J_{vol,act} = (A_p/A_{p,ref}) \quad J_{vol,pot} \tag{35}$$

$J_{vol,act}$ actual amount of pesticide volatilisation, kg/(m^2 d)

f_{mas} factor for the effect of pesticide mass on the plants

A_p areic mass of pesticide on the plants, kg/m^2

$A_{p,ref}$ reference areic mass of pesticide on the plants, 1.0 10^{-4} kg/m^2 (= 1 kg/ha).

Photodegradation

The amount of pesticide transformation by solar irradiation is described by first-order kinetics:

$$R_{ph} = k_{ph} \, A_p \tag{36}$$

R_{ph} amount of photo transformation on the leaves, kg/(m^2 d)

k_{ph} rate coefficient of photo transformation, 1/d

The rate coefficient k_{ph} is set dependent on sunlight irradiation intensity:

$$k_{ph} = \left(\frac{I_{act}}{I_{ref}} \right) k_{ph,ref} \tag{37}$$

I_{act} actual solar irradiation intensity, W/m^2

I_{ref} reference solar irradiation intensity, (*e.g.,* 500 W/m^2)

$k_{ph,ref}$ rate coefficient of photo transformation at reference irradiation intensity, 1/d

The coefficient $k_{ph,ref}$ is one of the quantities to be calibrated in the computation on the basis of the measurements or it has to be derived from other studies with the respective pesticide.

If two deposit fractions on plants, well-exposed and poorly-exposed, have been defined (see 2.5.1) all processes will be reduced linearly for the poorly exposed fraction as shown in the following equation.

$$k_{w,p} = k_w \cdot f_{w,p} \tag{38}$$

$$k_{pen,p} = k_{pen} \cdot f_{pen,p} \tag{39}$$

$$k_{ph,p} = k_{ph} \cdot f_{ph,p} \tag{40}$$

$$J_{Vol,act,p} = J_{Vol,act} \cdot f_{Vol,p} \tag{41}$$

$k_{w,p}$	coefficient for pesticide wash-off for the poorly exposed fraction [1/mm]
$k_{pen,p}$	rate coefficient of penetration for the poorly exposed fraction [1/d]
$k_{ph,p}$	rate coefficient of photo transformation for the poorly exposed fraction [1/d]
$J_{vol,act,p}$	actual rate of pesticide volatilisation, kg/(m^2 d)
$f_{w,p}$	reduction factor to correct for the poorly exposed wash-off fraction [-]
$f_{pen,p}$	reduction factor to correct for the poorly exposed penetration fraction [-]
$f_{Ph,p}$	reduction factor to correct for the poorly exposed transformation fraction [-]
$f_{Vol,p}$	reduction factor to correct for the poorly exposed volatilisation off fraction [-]

2.5.4 Soil surface

2.5.4.1 Volatilisation from soil surfaces

To estimate the amount of pesticide which is transferred from the soil surface to the atmosphere (volatilisation) the assumption is made that the concentration of the pesticide in the air above the soil is negligibly low. However, before the pesticide is released it has to diffuse through a small boundary layer which has to be given as user input. For this transfer two steps each characterised by a resistance r are considered: r_a is the resistance for transport through the boundary air layer and , r_s the resistance for diffusion through the top boundary soil layer.

$$J_{Volat} = \cdot \frac{c_{air}}{r_a + r_s} \tag{42}$$

J_{Volat}: volatilisation flux [g / (d cm²)]

c_{air}- concentration in soil air (top soil) [g/cm^3]

r_a: resistance for diffusion through the top boundary air layer (d/cm)

r_s: resistance for diffusion through the top boundary soil layer (d/cm)

The resistance r_a is calculated using the diffusion coefficient in air and the boundary air layer

$$r_a = \cdot \frac{d_a}{D_{air}} \tag{43}$$

D_{air}: diffusion coefficient in air [cm²/d]

r_a: resistance for diffusion through the top boundary air layer (d/cm)

d_a: boundary air layer (cm)

The resistance r_s is calculated using the diffusion coefficient in air and the boundary air layer

$$r_{a,s} = \frac{d_a}{D_{air}} \qquad (44)$$

D_{air}: diffusion coefficient in air [cm²/d]

$r_{a,s}$: resistance for diffusion through the top boundary soil layer (d/cm)

d: boundary air layer (cm)

$$r_s = \cdot \frac{0.5\, d_{top}}{D_{air}} \qquad (45)$$

D_{air}: diffusion coefficient in air [cm²/d]

r_a: resistance for diffusion through the top boundary air layer (d/cm)

d_{top}: top soil layer (fixed to 0.1 cm)

$D_{soil\ air}$ is corrected for temperature and soil moisture (see chapter 2.5.8).

2.5.4.2 Soil photolysis

PELMO is able to estimate soil photolysis which may be relevant shortly after application when the substance is still at the soil surface and exposed to sunlight. Usually, the soil photolysis is significant only for the time between application and first rainfall (or irrigation) event after the application because afterwards the substance has been transported to deeper soil layers where it would be not affected by sunlight any more.

To estimate the photo degradation, daily radiation must be known in addition to the photo-degradation rate at reference conditions (e.g. at 500 W/m²). The calculation is done according to following equation:

$$k_{phot} = \frac{100 - SC}{100} \cdot k_{phot0} \cdot \frac{I_{act}}{I_{ref}} \qquad (46)$$

k_{phot}: actual photo-degradation rate (1/d)

k_{phot0}: photo-degradation rate at reference condition (1/d)

I_{Ref}: radiation at reference condition (W/m²)

I_{act}: actual radiation (W/m²)

SC: crop interception factor (%)

Soil photolysis can be used to calculate the formation of primary metabolites Met A1 to Met D1.

Crop interception is used in the equation to account for the effect of shading by the crop. The information on daily radiation is usually expressed in energy per area and time (e.g. kJ/m²/d). Transformation into W/m² is done according to following equation.

$$I_{act} = 1000 * R / DL \qquad (47)$$

I_{act}: actual radiation (W/m²)

R: daily radiation (kJ/m²/s = kW/m²)

DL: number of seconds per day (s) = 86400 s

2.5.5 *Transport in soil*

2.5.5.1 Freundlich equilibrium sorption

The Freundlich equation is used to describe the sorption of pesticides in the equilibrium phase.

$$C_{ADS} = k_f \; C_{SOL}^{\;1/n} . \qquad (48)$$

C_{ADS} = concentration sorbed in soil (mg/kg)

k_F = equilibrium Freundlich sorption coefficient (L/kg)

C_{SOL} = concentration in the dissolved phase (mg/L)

$1/n$ = Freundlich exponent (-)

If no sorption coefficient (k_F -values) is available, the model estimates k_F -values based on the k_{FOC}-value, the sorption coefficient related to the organic carbon content in soil:

$$k_F = \frac{k_{FOC} \cdot OC}{100} \tag{49}$$

k_F: Freundlich sorption coefficient (L/kg)

OC: organic carbon content [%]

So PELMO calculates specific k_F:-values for all soil horizons by relating the sorption constant to the organic carbon content of the respective soil horizon.
In PELMO the Freundlich equation is limited to a lower trigger concentration which can be entered by the user. If the pesticide concentration is below the minimum concentration, a constant kd-value (calculated with the minimum concentration) will be used.

2.5.5.2 Transport in soil water when bound to dissolved organic carbon

PELMO is able to consider the transport of substances when bound to dissolved organic carbon (DOC) in soil water. The very simple model technically reduces the sorption constant by a factor which depends on the DOC content in soil water (which is assumed to be constant in the whole soil profile) and the equilibrium constant for the substance – doc – complex. Following equation is used:

$$k_{F,DOC} = \frac{k_F \cdot OC}{\left(1 + 10^6 \cdot DOC \cdot k_{DOC}\right) \cdot 100} \tag{50}$$

$k_{F,DOC}$: corrected Freundlich sorption coefficient after forming a DOC-complex (L/kg)

k_F: Freundlich sorption coefficient (L/kg)

OC: organic carbon content [%]

DOC: Dissolved organic carbon content (mg/L)

K_{DOC}: DOC complex formation constant (L/kg)

2.5.5.3 pH-dependent sorption

Some pesticides (usually weak acids) are characterised by significant dependency of sorption on pH in soil. Background is the dissociation into ionic species which is also dependent on pH. Equilibrium conditions between the neutral and the ionic form are calculated based on the pK$_a$ value.

$$K_a = \frac{[A^-][H_3O^+]}{[H-A]} \qquad pK_a = -\log(K_a) \tag{51}$$

$[H\text{-}A]$: equilibrium concentration of the neutral form pesticide (mol/L)

$[A^-]$: equilibrium concentration of the dissociated form of the pesticide (mol/L)

$[H_3O^+]$: equilibrium concentration of hydrogen ion (mol/L)

K_a: equilibrium constant (-)

Considering the mass balance of both species in soil

$$[A^-] + [H\text{-}A] = H\text{-}A \tag{52}$$

$H\text{-}A$: total concentration of the pesticide in soil (mol/L)

The above equation can be easily transformed into following expression:

$$f_{H-A} = \frac{[H-A]}{H-A} = \frac{[H_3O^+]}{K_a + [H_3O^+]} = \frac{10^{-pH}}{10^{-pH} + 10^{-pK_a}} \tag{53}$$

$f_{H\text{-}A}$: fraction of the neutral form in soil (pH-dependent)

If the soil pH in the sorption study and the soil pH used in the PELMO simulation are different the fraction of non-dissociated species $f_{H\text{-}A}$ will be different, too.

The following describes the situation under the laboratory sorption test:

$$f_{H-A,\exp} = \frac{10^{-pH,\exp}}{10^{-pH,\exp} + 10^{-pK_a}} \qquad (54)$$

$f_{H\text{-}A,exp}$ fraction of the neutral form in the laboratory soil

The next equation describes the situation in the computer simulation:

$$f_{H-A,sim} = \frac{10^{-pH,sim}}{10^{-pH,sim} + 10^{-pK_a}} \qquad (55)$$

$f_{H\text{-}A,sim}$ fraction of the neutral form in the computer simulation

The pH-dependent fractions of both forms are presented in Figure 5 for a pKa of 5.

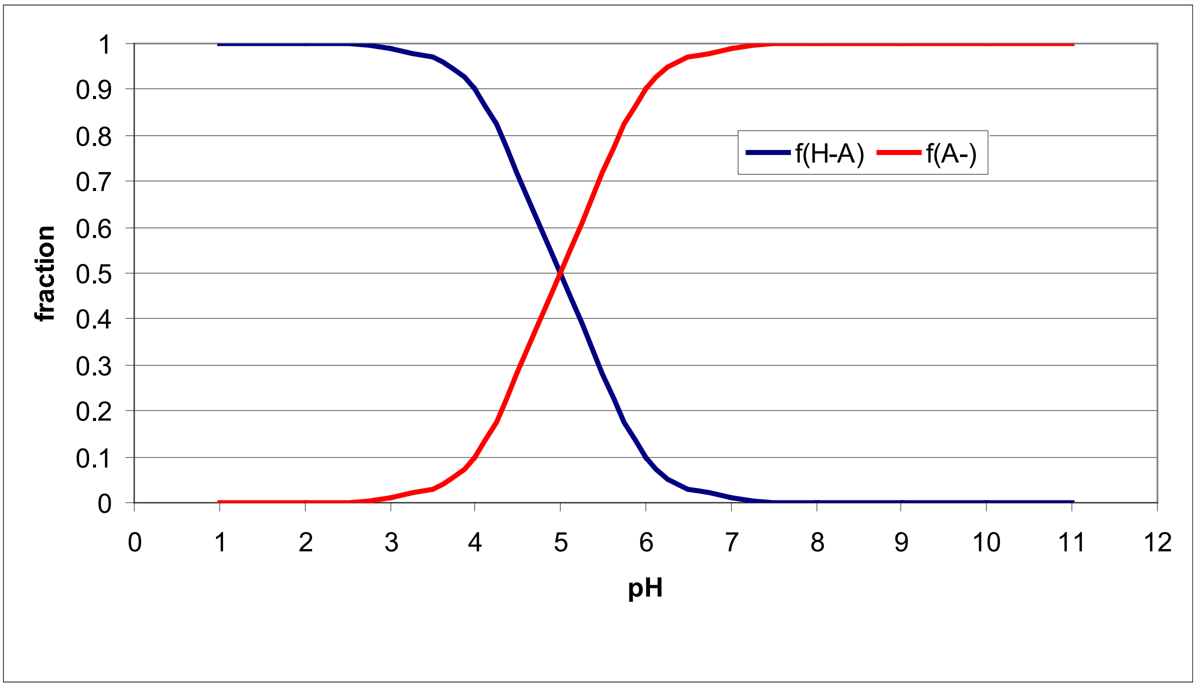


Figure 5: Distribution of (an)ionic and neutral form for a compound with pKa=5

PELMO estimates the sorption constant of the compound by the weighted mean of the two species and differences in the sorption constant at different pH-values are related to differences in $f_{H\text{-}A}$:

$$k_{FOC} = f_{H\text{-}A} * k_{FOC,H\text{-}A} + (1\text{-}f_{H\text{-}A}) * k_{FOC,A\text{-}} \quad (56)$$

k_{FOC}:	sorption constant of the compound (L/kg)
$f_{H\text{-}A}$:	fraction of the neutral form in soil (pH-dependent)
$k_{FOC,H\text{-}A}$:	sorption constant of the neutral form of the compound (L/kg)
$k_{FOC,A\text{-}}$:	sorption constant of the ionic form of the compound (L/kg)

Based on the previous equations the K_{FOC} values can be calculated for any soil pH if the pKa and the sorption constant is known for at least 2 different pH-values.

An example is given in Figure 6 (pKa: 5, pH 4: K_{FOC}: 500 L/kg, pH 8: K_{FOC}: 10 L/kg)

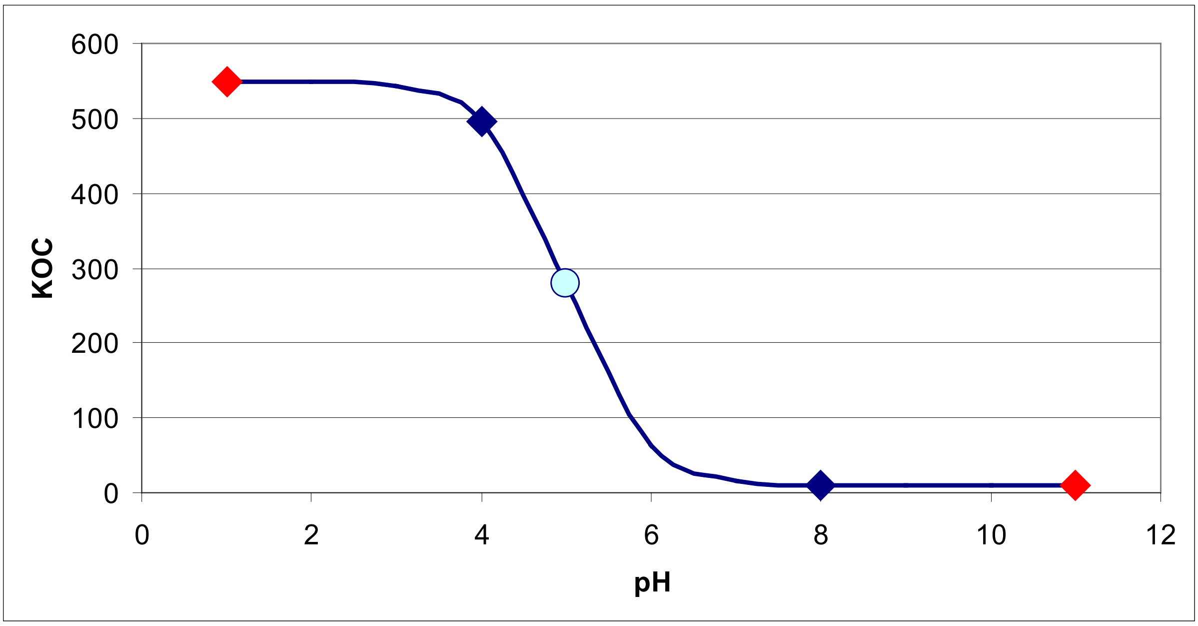


Figure 6: Overall sorption constant ($k_{f,OC}$) due to different sorption behaviour of ionic and non-ionic species for a compound with pKa=5

In Figure 6 the blue squares represent the sorption constant at two known pH values, the light blue circle the calculated sorption at the pKa-value (pH 5), where the fraction of ionic and neutral form are both 50 %, and the red squares show the calculated sorption constant for the pure ionic and neutral form of the molecule respectively.

To calculate sorption constants of this type of compounds PELMO 5 has 2 different built in models which refer to the equations mentioned earlier:

A K_{oc} is known at two different pH-values

All information necessary to calculate the K_{FOC} dependent on soil pH is available.

B K_{oc} is known at a single pH-value only

The calculation of sorption constant is only possible when considering at least one additional assumption.

It is known for the anions of weak acids that their sorption coefficients are two to three orders of magnitude lower than the coefficient of the non-ionic species (Nicholls, 1988). Therefore a fixed ratio of 1000:1 for the sorption constants of the neutral and the ionic form is considered to overcome the missing information. Based on this assumption, which is of course only a rough estimation, the sorption constant can be calculated for any given soil pH.

2.5.5.4 Kinetic (non-equilibrium) sorption

The previous versions of PELMO were limited to equilibrium conditions using the Freundlich equation. However, long-term or aged sorption is a process that was found to be a relevant process for the environmental fate behaviour of pesticides (Boesten, 1989). Therefore, transport experiments of pesticides in soil cannot be described adequately by assuming equilibrium sorption with Freundlich parameters derived from the study OECD 106 (OECD 2000). The relevance of aged sorption is extensively discussed in FOCUS, 2014 where also guidance is given how to parameterize models accordingly.

Therefore, in PELMO 5 additional routines have been implemented that are able to describe non-equilibrium or kinetic sorption processes (Klein 2009). The realisation is based on a two-stage/one-rate-model assuming that the equilibrium sorption of a substance can be distinguished from non-equilibrium type sorption by assuming two different types of sorption sites in soil.

Generally, additional parameters have to be defined to describe the sorption isotherm for the non-equilibrium sites, and parameters that describe the adsorption and desorption rates between the equilibrium and non-equilibrium sites. As default degradation in the non-equilibrium domain is assumed negligible (FOCUS, 2009) but an additional degradation rate other than zero can be specified for the non-equilibrium sites.

The same algorithm as in FOCUS PRZM 3.5.2. was used.

A simple model for dealing with sorption kinetics is the two-site/ one rate model (Van Genuchten and Wagenet, 1989; Streck et al., 1995), which differentiates equilibrium and non-equilibrium sorption sites. The basis for this simplification is the assumption that short-term kinetic sorption processes reaching sorption equilibrium within 1-2 days and usually measured following the OECD 106 guidance can be described by sorption equilibrium whereas long-term sorption equilibrium requires much more time. The two-site sorption and degradation kinetics model assumes two types of soil fractions (sites) coexisting in a soil representative elementary volume, with one adsorbing chemicals instantaneously and the other time-dependently (FOCUS 2009).

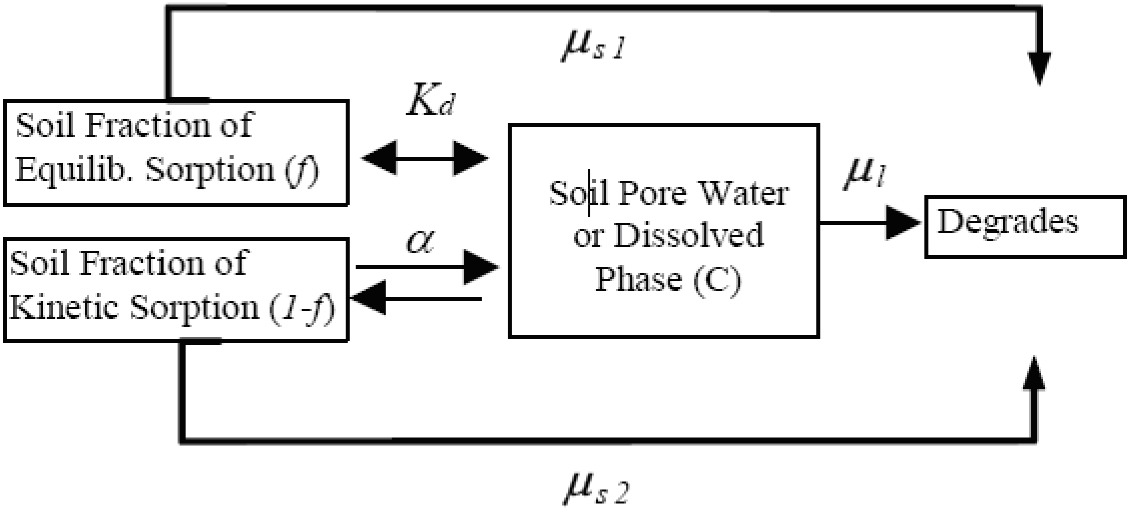


Figure 7: Diagram of equilibrium and non-equilibrium domains of the soil system (kinetic processes shown as →, distribution processes shown as ↔)

FOCUS (2009) describes three methods to simulate kinetic sorption in soil

- The PEARL-approach
- The Streck –approach (implemented in PRZM)

The models are different with respect to the definition of the total concentration adsorbed. However, as shown by FOCUS (2009) the models are mathematically equivalent, because they describe the same process and the parameters derived using one of the models can be transferred into parameters of the other. The STRECK-model was implemented in the simulation model PELMO, but automatic transformation of input parameters in the PELMO shell makes it possible to consider kinetic sorption parameters according to the PEARL approach.

Degradation processes at non-equilibrium sites follow 1st order kinetics with a specific rate constant, but same moisture, depth and temperature dependency as at the equilibrium sites. It is also possible to run simulations where degradation in the non-equilibrium domain is switched off.

The new code was programmed considering the following differential equation system (Chen and Wagenet, 1997):

1. Differential Equations

The differential equations and initial conditions are

$$\frac{d}{dt}\left[\theta C + \rho\left(S_1 + S_2\right)\right] = -\mu_1 \theta C - \left(\mu_{S_1}\rho S_1 + \mu_{S_2}\rho S_2\right) \qquad (57)$$

$$\frac{dS_1}{dt} = fKd\,\frac{dC}{dt}$$

(58)

$$\frac{dS_2}{dt} = \alpha\left[\left(1 - f\right)K_d C - S_2\right] - \mu_{S_2} S_2$$

(59)

With the initial conditions

$$C(0) = C_0$$

$$S_1(0) = fK_d C_0$$

$$S_2(0) = S_0$$

C:	Concentration in the dissolved phase (µg/mL)
C_t:	total Concentration in the soil (µg/mL)
S_1	Concentration in the instantaneous (equilibrium) adsorbed phase (µg/g)
S_2 :	Concentration in the kinetic adsorbed phase (µg/g)
f	Soil fraction of the instantaneous adsorbed phase (-)
K_d	Partition coefficient when adsorption/desorption equilibrium achieved (mL/g)
a	First-order desorption rate constant in the kinetic adsorbed phase (day^{-1})
μ_{S1}:	Degradation rate constant on the equilibrium adsorption site (day^{-1})
μ_{S2}:	Degradation rate constant on the kinetics adsorption site (day^{-1})
μ_1	Degradation rate constant in the soil pore water or liquid phase (day^{-1})
θ :	Volumetric soil moisture content (cm³/cm³)

ρ: Soil bulk density (g/cm³)

t: Time (day)

The analytical solutions for these equations are described in detail in Annex A.

The whole implementation of kinetic sorption is based on linear sorption. Since PELMO is calculating sorption in soil according to the non-linear Freundlich approach which means that sorption is dependent on the concentration of the substance in the soil solution. The corresponding partitioning coefficient (K_d-value) is derived at the relevant concentration.

using a stepwise approach which recalculates the sorption equilibrium in soil following the changes in concentration caused by kinetic sorption.

Since the time step of maximum one day in PELMO is by minimum one order of magnitude smaller than the sorption rate coefficient (typically in the range of 0.01 1/d) the numerical errors can be considered very small.

2.5.5.5 Sorption at dry moisture condition

Comparisons with experimental data (Vanclooster et al. 2003a and 2003b) showed that the volatilisation from soil surfaces is often overestimated at dry soil moisture conditions which could be caused by increased sorption at low soil moisture conditions. PELMO does not consider increased sorption at low soil moisture but modifies the Henry's law constant as described in Section (2.5.8.3).

2.5.5.6 Dispersion in soil

The algorithms in PELMO will always lead to numerical dispersion. The respective dispersion length is linearly dependent on the compartment size defined in the scenario according to following equation:

$$DL = 0.5 * d \qquad (60)$$

DL: dispersion length (cm)

d: thickness of soil compartments (cm)

Additionally dispersion in the soil column can be considered explicitly either by dispersion lengths or by dispersion coefficients.

Dispersion coefficient and dispersion length are linked parameters. A constant dispersion coefficient defined by the user results in dynamic dispersion lengths and constant dispersion length to respective dynamic dispersion coefficients according to the following equation:

$$DL = DC / v \qquad (61)$$

DL: dispersion length (cm)

DC: dispersion coefficient (cm²/d)

v: pore water velocity (cm/d)

To correct for the implicit numerical dispersion PELMO uses following equation:

$$DC_{dyn} = (DL - d * 0.5) * v \qquad (62)$$

DC_{dyn}: new variable dispersion coefficient in PELMO (cm²/d)

DL: dispersion length (cm)

d: thickness of soil compartments (cm)

v: pore water velocity (cm/d)

To avoid negative dispersion coefficients the equation is used only if the dispersion length is greater than 50% of the selected compartment size. Otherwise the user has to reduce the compartment size.

2.5.5.7 Macropore flow

In PELMO a very simple descriptive approach to consider macropore flow is implemented. The concentration of pesticide entering macropores at the soil surface is calculated using the mixing depth concept, whereby incoming rainfall is assumed to mix perfectly with the resident water in a shallow surface layer of soil. Only pesticide residues in the surface layer (i=0) and the first soil layer (i=1) are available for this process. Consequently, the mixing depth is the sum of the surface layer and the first soil layer.

The flux of pesticide into the macropores is given by the pesticide mass per area in the respective soil layer, the amount of water routed into macro pores, y the pesticide mass multiplied by the infiltration rate into macropores I_{ma}, and this amount of pesticide is extracted from the mass in the matrix to maintain the mass balance.

$$J_{ma} = \frac{I_{ma}}{(d_0 + d_1)} \sum_{i=0}^{1} \frac{m_i \; d_i}{(I_i + \Theta_i \; d_i)} \tag{63}$$

m_i: areic pesticide mass in layer *i* (g/cm²)

d_i: Depth of layer *i* (cm)

I_{ma}: Amount of water routed into macropore (cm), see equation (20)

I_i: Amount of water infilitrated into soil layer *i* (cm d^{-1})

Θ_i: volumetric soil water content of layer *i* (cm³/cm³)

J_{ma}: Flux of pesticide into the macro pore (g/cm^{-2} d^{-1})

A fixed depth needs to be defined of the macropores. At that soil depth percolate is distributed in the soil matrix system again independent of the actual soil moisture conditions.

Above that depth there is no exchange between the macropore and micropore domain. Substance is directly transported within one day from the surface (where the macro pore is filled with water and substance) to the bottom of the macro pore (where water and substance is released into the micro pore system).

2.5.6 Plant uptake via roots

PELMO considers the plant uptake of compounds via the root system based on a plant uptake factor (PUF), the concentration in soil water and the transpiration stream according to following equation:

$$\frac{dm_{i,uptake}}{dt} = PUF\ c_{i,sw}\ T_i \qquad (64)$$

PUF: Plant Uptake Factor [-]

$m_{i,uptake}$: substance mass taken up by plants [mg/d]

$c_{i,sw}$: concentration of the compound in soil water of layer i (mg/L)

T_i: water taken up by plants out of layer i (L/d)

Please consider that the PUF is determined in experiments where often a difference between the plant uptake factor and the transpiration stream concentration factor (TSCF) is determined. In these experiments the TSCF describes the uptake via roots into the shoots whereas the PUF describes the uptake into the roots. PELMO does not distinguish between roots and stem. In so far it is up to the user whether for the parameter PUF in PELMO the experimental PUF or experimental TSCF is set.

2.5.7 Transformation in soil

PELMO allows calculations of pesticide degradation based on single first order kinetics (SFO) for all soil horizons:

$$\frac{dc}{dt} = -k_{total} \cdot t \qquad (65)$$

k_{total}: total rate constant [1/d]

t: time [d]

c: concentration of the pesticide (mol/L)

The total rate constant is usually obtained in laboratory experiments under constant conditions. However, dependent on depth, temperature, soil moisture and daily fluctuations the total rate constant is corrected on each simulation day.

$$k_{total} = k_0 \cdot f_{temp}\, f_{moisture}\, f_{depth}\, f_{day} \qquad (66)$$

k_{total}: total rate constant [1/d]

k_0: rate constant under standard conditions [1/d]

f_{temp}: temperature correction factor (-)

f_{moist}: moisture correction factor (-)

f_{depth}: depth correction factor(-)

f_{day}: correction factor due to daily temperature fluctuations (-)

The differential equation can be easily solved:

$$c(t) = c_0 \cdot e^{-kt} \qquad DegT_{50} = \frac{\ln(2)}{k} \qquad (67)$$

c_0: Initial concentration of the pesticide (g/cm³)

$DegT_{50}$: Half life of the pesticide (d)

Usually pesticides are transformed to different products (metabolites). PELMO 5 can handle up to 4 direct and additional 4 sequential transformation products. For each compound also a sink compartment (complete mineralisation or formation of bound residues can be considered by PELMO.

The above mentioned overall transformation rate of a substance is defined as the sum of all partial transformation rates of the respective compound.

$$k_{total} = k_{BR,CO_2} + \sum_{met=1}^{n} k_{met} \qquad (68)$$

k_{met}: specific degradation rate to metabolite *met*

$k_{BR,CO2t}$: degradation rate to bound residues / CO_2

As transformation in soil is dependent on soil depth, temperature and soil moisture PELMO allows is able to take this into account:

2.5.7.1 Depth dependency

Depth dependent biodegradation factors can be defined for each soil horizon and for each transformation product.

2.5.7.2 Temperature dependency

Transformation rate constants depend on soil temperature. PELMO 5 uses the Q10-rule to consider the dependency:

$$f_{Temp} = Q^{\frac{T-T_0}{10}} \tag{69}$$

f_{temp}: temperature correction factor

Q: factor for rate increase given a temperature increase of 10 °C

T_0: reference temperature for degradation (e.g. 20 °C)

T: actual soil temperature (°C)

A given increase of temperature will always lead to the same increase of degradation. This equation is commonly used to describe temperature dependency of chemical or biological reactions. The user has to enter the increase factor Q_{10} as well as the reference temperature (e.g. temperature of the degradation test).

Due to the exponential influence of the temperature on the degradation rate, the increase in the degradation constant given a temperature increase is higher than the decrease of the constant due to a corresponding temperature decrease. For this reason, the use of the daily (arithmetic) mean temperature on days with high temperature fluctuations leads to an underestimation of the actual degradation behaviour. Increased degradation as a result of this non-linear effect has been incorporated in the PELMO model.
The correction is calculated according to the following equation, assuming that the temperature fluctuation within a day exhibits a sinusoidal curve:

$$f_{day} = \frac{\int_{x=0}^{2\pi} Q^{\frac{T_{act} S \cdot \sin(x) - T_0}{10}}}{2\pi} dx \qquad (70)$$

f_{day}: influence of intra day's fluctuation of the soil temperature

T_{act}: *average soil temperature (°C)*

T_0: *standard temperature (°C)*

S: daily temperature fluctuation $(T_{max}-T_{min})/2$

The integral is numerically solved by using ten minutes time increments with constant temperature each.

2.5.7.3 Moisture dependency

Transformation rate constants depend on soil temperature. PELMO 5 uses the Walker model [Walker 1978, Walker and Barnes 1981] to consider the dependency:

Two different variations for soil moisture correction can be used:

- correction based on absolute soil moisture

$$f_{moist,met} = \left(\frac{\Theta}{\Theta_0} \right)^{f_W} \qquad (71)$$

$f_{met,\Theta}$: soil moisture correction factor for the transformation to met (-)

Θ: current volumetric soil moisture in the respective soil layer (%)

Θ_0: moisture during the biodegradation test (%)

f_W: exponent describing the moisture dependency (-)

- correction based on relative soil moisture (related to field capacity)

$$f_{moist,met} = \left(\frac{100 \cdot \Theta}{\Theta_{FC} \cdot f_0} \right)^{f_W} \qquad (72)$$

$f_{moist,met}$: soil moisture correction factor for the transformation to *met* (-)

Θ: current volumetric soil moisture (cm³ cm^{-3})

Θ_{FC}: soil moisture at field capacity (cm³ /cm^3)

f_0: soil moisture percentage of field capacity during the biodegradation test (%)

f_W: exponent describing the moisture dependency (-)

2.5.8 Transport in soil air

PELMO is able to consider distribution and transport in soil air. Distribution is calculated based on Henry’s law constant, transport in air based on Fick’s law.

$$J_{gas} = -D_{air} \cdot \frac{c_{air}}{d} \qquad (73)$$

J_{gas}: mass rate for transport in soil air [g / (d cm²)]

D_{air}: diffusion coefficient in air [cm²/d]

c_{air}- concentration in soil air (top soil) [g/cm^3]

d: the distance between the centre of two neighboured compartments (cm)

The diffusion coefficient in air is corrected for temperature according to following equation:

$$D_{air} = D_{air,20\,°C} \cdot \left(\frac{T_{soil}}{T_{0,soil}} \right)^{1.75} \qquad (74)$$

D_{air}: diffusion coefficient in air [cm²/d]

T_{soil} actual soil temperature (K)

$T_{0,soil}$: reference soil temperature (293 K or 20 °C)

The diffusion is further corrected for actual soil moisture considering Millington and Quirk (1960) using the parametrisation of Jin and Jury (1996):

$$D_{\text{soil air}} = D_{\text{air}} \cdot \frac{\Theta_{\text{air}}^{2}}{\Theta^{2/3}} \tag{75}$$

D_{air}: diffusion coefficient in air [cm^2/d]

$D_{soil\ air}$ diffusion coefficient in soil air [cm^2/d]

Θ_{air} volumetric air content in soil (cm^3/cm^3)

$T_{0,soil}$: reference soil temperature (at 293 K or (20 °C)

2.5.8.1 Distribution in soil air

Distribution in soil air is calculated based on Henry's law constant according to the following equation:

$$H = \frac{P \cdot M}{C_S} \qquad H' = \frac{H}{R\,T} \tag{76}$$

H: *Henry's law constant [J/mol]*

H': *Henry's law constant (dimensionless)*

P: *vapour pressure [Pa]*

M: *molecular mass [g/mol]*

C_S *water solubility [mg/L]*

Water solubility and vapour pressure are assumed to be dependent on the temperature. It is assumed that the increase of these parameters are constant for a given temperature increase (e.g. 10 °C). That will double the Henry's law constant if the temperature increase is 10 °C. The concentration of the pesticide in the gas phase is calculated based on the concentration in the soil water according to the following equation:

$$C_{Air} = (\Theta_{FC} - \Theta) \cdot c_{dis}\ H' \tag{77}$$

Θ_{FC}: soil moisture at field capacity (cm^3 /cm ^{3})

C_{Air}: concentration in soil air (g/cm^3)

c_{dis}: concentration in soil water (g / cm^3)

2.5.8.2 <u>Temperature dependency of Henry's law constant</u>

PELMO 5 considers a temperature dependent Henry's law-constant. H must be known at two different temperatures. PELMO will use these values to extrapolate the H for any given temperature according to the following equation, which assumes constant increasing factors for Henry's law constant for a given increase of air temperature.

$$f_{Temp,met,H} = Q_{10,H}^{\frac{T-T_1}{10}} \qquad Q_{10,H} = 10^{\frac{Log(\frac{H_2}{H_1})}{\frac{T_2-T_1}{10}}} \tag{78}$$

$f_{Temp,H}$: temperature correction factor for the Henry’s law constant

$Q_{10,H}$: factor for rate increase given a temperature increase of 10 °C

H_0: Henry’s law constant at temperature T_i (J/mol) (e.g. 20 °C)

T: dynamic soil temperature (°C)

H_i: Henry’s law constant at temperature T_i (J/mol)

T_i: Temperature i (°C)

2.5.8.3 <u>Henry’s law constant at dry soil moisture conditions</u>

Comparisons with experimental data (Vanclooster et al. 2003a and 2003b) showed that the volatilisation from soil surfaces is often overestimated at dry soil moisture conditions.
To compensate the overestimation PELMO 5 reduces the Henry’s law constant when soil moisture in the top mm is below wilting point according to following equation:

$$H_{corr} = H_i \cdot \frac{RH_{WP} - RH}{RH_{WP} - RH_{AD}} \cdot f_{AD} \tag{79}$$

H_{corr}: Henry’s law constant corrected for soil moisture below wilting point

f_{AD}: Reduction of Henry’s law constant when soil is air dried (equivalent to “increase of sorption when soil is air dried)

RH: current relative humidity in air at the soil surface (%)

RH_{WP}: relative humidity in air at the soil surface if soil moisture is at wilting point (%)

RH_{AD}: relative humidity in air at the soil surface if soil moisture is air dried (%)

2.5.8.4 Diffusion in the soil air

PELMO estimates the diffusion between two different soil layers according to Fick's law:

$$J_{Diff,air} = -D_{air} \cdot \frac{dc}{dx} \tag{80}$$

J_{Dif}: mass rate for diffusion in soil air [g /(d cm^2)]

D_{air}: diffusion coefficient in air [cm²/d]

$\frac{dc}{dx}$ gradient of concentration in soil air [g /cm^4]

2.5.9 Run-off and soil erosion

PELMO is able to calculate the loss of pesticide due to run-off after storm events. PELMO uses the '*USDA Soil Conservation Service curve number approach*' (Haith and Loehr 1979). Depending on soil type, land use and management practices the run-off is calculated empirically (see section 2.3.5). The standard equation for calculating the amount of pesticide in run-off only requests the pesticide concentration in the soil water of the surface layer and the daily run-off depth. However, in the course of harmonisation of model results between PRZM and PELMO (FOCUS 2000) an additional modification of the run-off module was implemented:

The calculation of run-off in PRZM-1 and PELMO 1.0 was assuming total portioning of rainfall with top soil water (e.g. top 5 cm). As shown by experimental data only part of the soil water is ideally mixed with rainwater and consequently only part of the chemicals present in soil water is actually washed-off. To more accurately account for the run-off process PRZM-3 uses 1 mm sub layers in the top 2 cm considering substance fraction of 70 % (top mm) down to 2.8 % (2 cm depth) available for run-off. They are calculated in PRZM-3 depth dependently according to following equation:

$$f_{Ro,i} = 0.7 \left(\frac{1}{(2 \cdot d_i) + 0.9} \right)^2 \tag{81}$$

$f_{Ro,i}$: fraction of chemical in soil water available for runoff in PRZM (-)

d_i: depth to midpoint of soil layer *i* (cm)

PELMO 3.0 considers the limited run-off availability aspect of the PRZM-3. In the surface layer it is fixed to 0.7 in accordance to PRZM. For the first soil layer it is calculated according to following equation

$$f_{Ro} = 0.15795\ \frac{2\ cm}{d_1}$$

f_{Ro}: fraction of chemical in soil water available for runoff in PELMO (-)

d_i: depth of first soil layer (cm)

The PELMO equation gives a fraction 6.4 % for 5 cm soil layers. The PRZM equation would result in an average fraction of 6.3% for the top 5 cm in soil. The amount of substances in runoff is then calculated according to following equation:

$$J_{Ro} = f_{Ro}\, Q \cdot c_{sw} \tag{82}$$

J_{Ro}: pesticide loss due to run-off [g /(cm^2 d)]

Q: daily run-off depth (cm d^{-1})

C_{sw}: pesticide concentration in soil water [g /cm^3]

f_{Ro}: fraction of chemical in soil water available for runoff in PELMO (-)

The equation for calculating the amount of pesticide transported via soil erosion is estimated based on the soil erosion and the amount of pesticide adsorbed at the top soil layer according to following equation:

$$J_{ER} = X_e \; r_{OM} \; k_d \; c_{sw} \qquad (83)$$

J_{ER}: pesticide loss due to soil erosion [$g \, cm^{-2} \, d^{-1}$]

r_{OM}: the enrichment ratio for organic matter ($g \, g^{-1}$)

X_e: the erosion sediment loss [$g \, cm^{-2} \, d^{-1}$]

C_{sw}: pesticide concentration in soil water [$kg \, L^{-1}$]

k_d: sorption constant [$L \, kg^{-1}$]

Because erosion is a selective process during runoff events, eroded sediments become "enriched" in smaller particles. This is considered by the enrichment ratio, $r_{OM.}$ The sediment transport theory available to describe this process requires substantially more hydraulic spatial and temporal resolution than used in PELMO-3, leading to the adoption of an empirical approach here.

2.6 Metabolites

PELMO is able to calculate the formation and transformation up to 8 transformation products (metabolites) including the formation bound residues and/or CO_2 (see the transformation scheme in Figure 8).

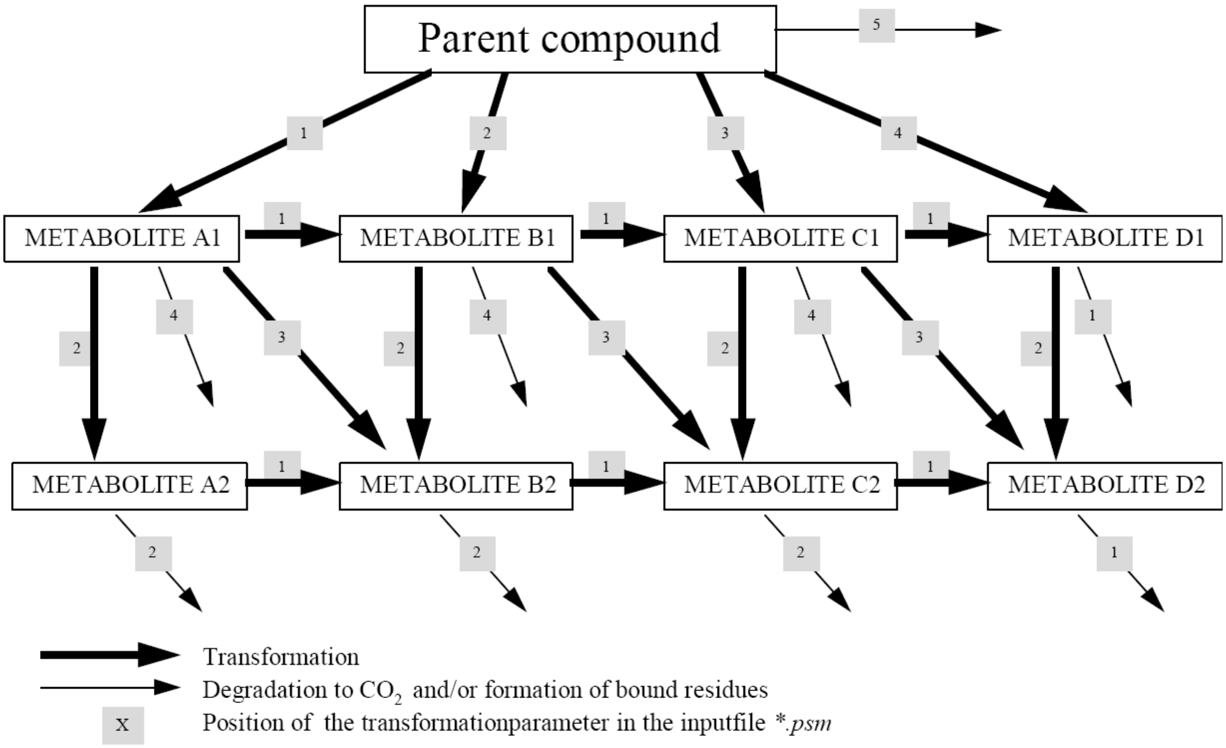


Figure 8: Transformation scheme realised in PELMO (taken from Jene 1998)

The leaching of metabolites is calculated for each metabolite separately considering special transformation- and sorption parameters for each metabolite. Corresponding to the calculation of the a.i. degradation in PELMO 2.01 (Arrhenius approach and Walker equation) individual Q10 and Walker-exponents can be defined for each metabolite.

As one substance can transform to different metabolites PELMO considers in total 5 different transformation pathways for the parent compound (including the mineralization and the formation of bound residues as a loss process). The overall transformation rate of a substance is always defined as the sum of all individual partial transformation rates.

As shown by the transformation scheme (Figure 8) most of the metabolites can be formed by more than one precursor. Thus, the formation of metabolites can be also defined as the sum of degradation processes from the different previous compounds (see 55):

$$F_{total,j} = \sum_{i=1}^{n} F_{i,j} \tag{84}$$

$F_{total,j}$: formation rate of metabolite j (day^{-1})

$F_{i,j}$: specific formation rate of metabolite j from precursor i

The variable “formation of metabolite j” represents the sum of all formation processes leading to metabolite j. Based on Ftotal the mass of transformation products is calculated for each time step in each soil layer.

Separate sorption coefficients k_f and Freundlich exponents can also be considered for each transformation product. However, simulation of direct application to plants or soil and volatilisation of metabolites (incl. transport in soil air) is not possible.

A molar mass correction is carried out after all transformation processes. Thus, metabolite concentrations are expressed based on their masses not as parent equivalents.

3 Working with PELMO

3.1 Installing PELMO

Perform following steps for the installation of PELMO:

1. Call the current PELMO installation file
2. Select a directory and start unzipping the files into a temp-folder
3. After unzipping close the installation package
4. Call setup.exe in the folder where the files were unzipped
5. PELMO may be un-installed using the standard MS-Windows un-install tools provided in the “Control Panel” under “Add/Remove Programs”.

3.2 File handling between PELMO.EXE and WPELMO.EXE

PELMO.EXE runs under *Microsoft DOS*. However, to make editing and creating of PELMO input files easier in a *Microsoft Windows* environment, a shell called WPELMO.EXE was built around PELMO.EXE.

The information necessary to run PELMO.EXE is divided in a number of input data files. The shell WPELMO.EXE allows creating or editing of these files by the user. For each simulation a single pesticide data file (extension: PSM), a single soil data file (extension: SOI), a single crop rotation file (extension: CRP) and a number of climate data files (extension: CLI) are necessary. However, for FOCUS-tier 1 -simulations only the pesticide data file needs to be created by the user; the scenario and climate data files are already defined and should not be modified.

When performing EFSA tier 3 soil simulations most of the input data are read from the transfer file of PERSAM, the PECsoil model which is used at the initial tiers. However, PERSAM does not deliver all PELMO input data (e.g. the Freundlich exponent is missing). These input parameters have to be modified manually, if the default values are not appropriate.

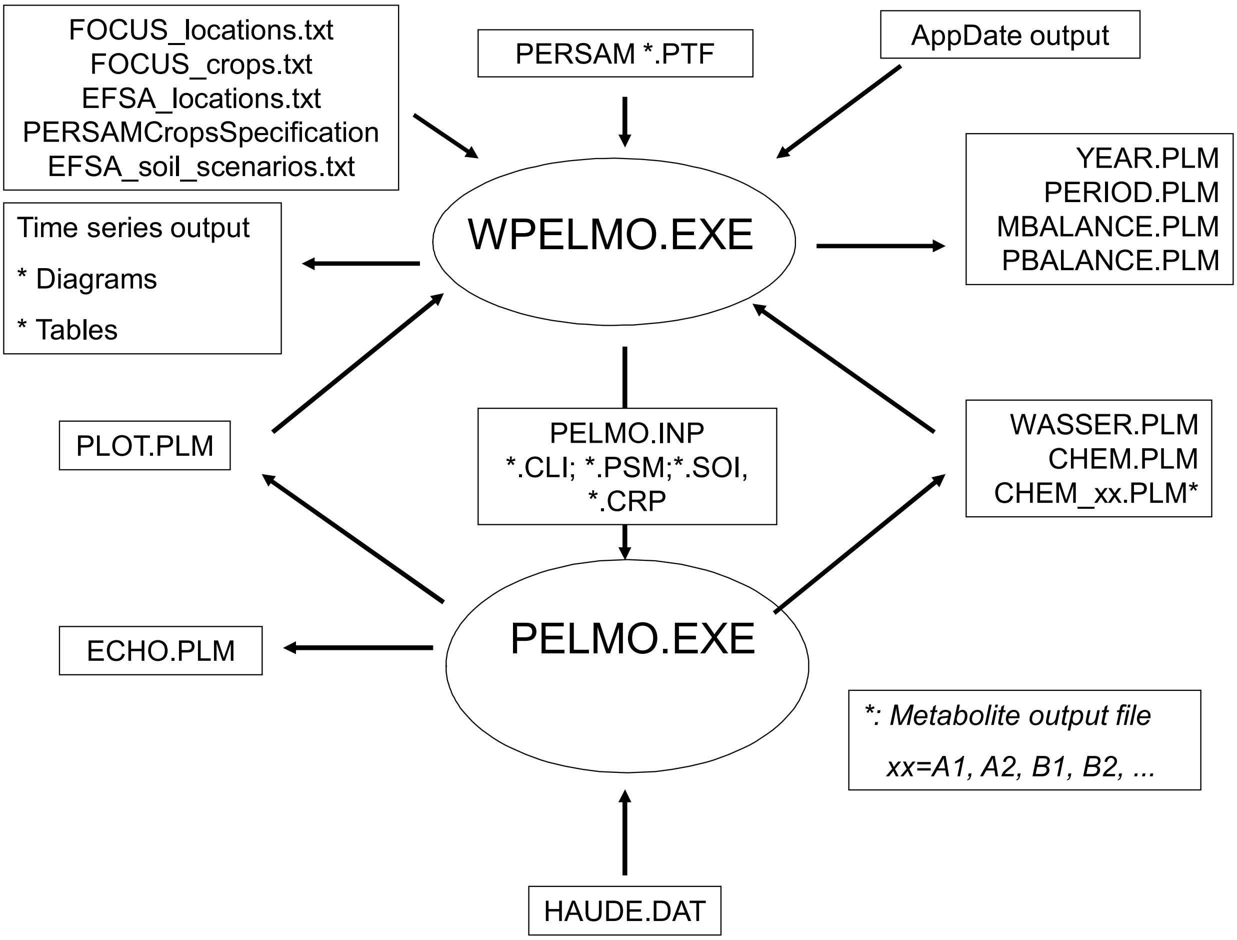


Figure 9: File handling between the simulation program PELMO.EXE and the shell WPELMO.EXE

Apart from EFSA Tier 3A PECsoil simulations the user starts a PELMO simulation by selecting the scenario (location and crop, possibly irrigation) and the pesticide data. For FOCUS simulations the required scenario and climate input data files (*.cli and *.sze) are automatically selected by the shell and written into a small ASCII file called PELMO.INP. This file will be read by the simulation program PELMO.EXE (see the figure).

In order to combine the FOCUS groundwater crops correctly with the FOCUS groundwater locations the two ASCII files FOCUS_crops.txt and FOCUS_locations are used by WPELMO. For the same reason the ASCII files EFSA_locations.txt, PERSAMCropsSpecification.txt and EFSA_soil_scenarios.txt are used for defining the EFSA PECsoil scenarios.

The file HAUDE.DAT contains the monthly Haude-factors. This information is not used for FOCUS-simulations. However, the file must be present in the FOCUS-directory of PELMO.

In the new version of PELMO there is an interface established which presents results of AppDate. AppDate is a tool that estimates suitable application dates based on the BBCH stages of the FOCUS groundwater crops. This interface is not an essential part of FOCUS

PELMO. However, if the necessary information is provided in the subfolder “AppDate” then the user will receive recommendations for the date of application.

Following files (All in ASCII format) should be present in the subfolder “AppDate” in order to enable the recommendations:

- BBCH_Châteaudun (H).out
- BBCH_Hamburg (H).out
- BBCH_Jokioinen (H).out
- BBCH_Kremünster (H).out
- BBCH_Okehampton (H).out
- BBCH_Piacenza (H).out
- BBCH_Porto (O).out
- BBCH_Sevilla (S).out
- BBCH_Thiva (T).out
- Crop_interception.out

The user has to place the files manually into the subfolder “AppDate”.

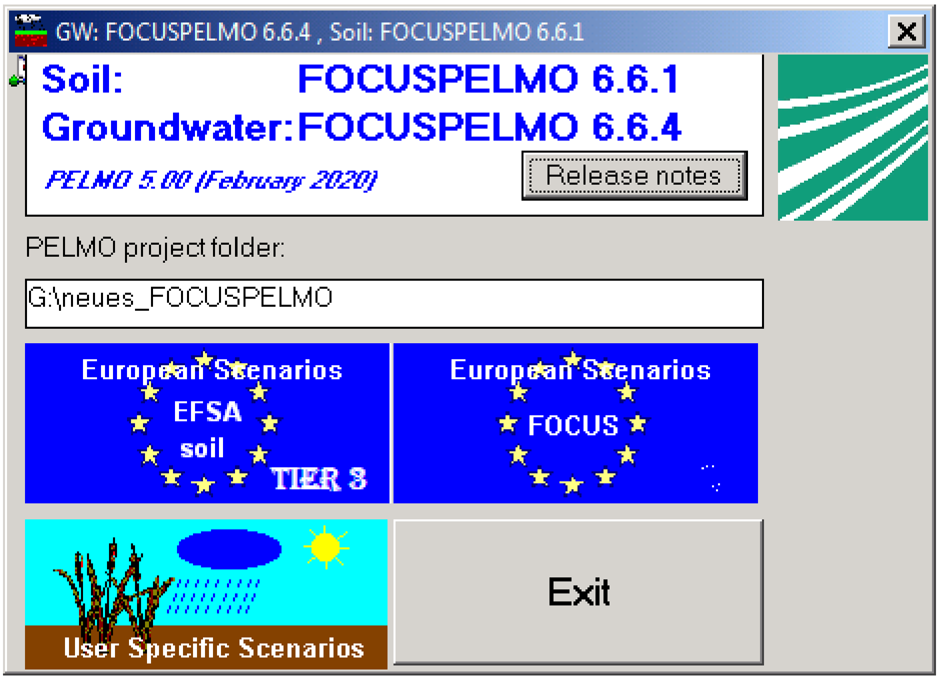
Please note, if this information is not present FOCUS PELMO will not fail, the recommendation option is then simply disabled. Please also note that these recommendations are not part of the normal FOCUS shell and can be updated independent on the actual FOCUS PELMO version. It is not part of FOCUS version control. This is because the recommendations are only suggestions which the user doesn’t need to follow.

During the simulation PELMO.EXE creates a number of output files:

- ECHO.PLM:	echo of all input parameters of the specific simulation
- WASSER.PLM:	hydrologic output data (tables)
- CHEM.PLM:	pesticide output data (tables)
- CHEM_xx:	metabolite output data (tables), xx=A1, A2, B1, B2, ...
- PLOT.PLM:	time series output file, used by WPELMO.EXE to create diagrams

When a PELMO simulation successfully terminates the annual average concentrations at 1 m depth and at the lower boundary of the defined soil profile are calculated by WPELMO.EXE based on the results written to WASSER.PLM (hydrology output), CHEM.PLM (pesticide output) and CHEM_xx (metabolite output). WPELMO also creates the files forMBALANCE.PLM and PBALANCE.PLM which contain the total annual mass balances for water (MPBALANCE.PLM) and for the pesticide/metabolites (PBALANCE.PLM). When having performed simulations using the EFSA PECsoil scenarios the shell creates additionally the file PECsoil_<soil depth>.plm.

After WPELMO has been loaded the form shown in Figure 10 is shown.



PELMO project folder: G:\neues_FOCUSPELMO

Figure 10: PELMO 5.0: Main screen

The flags are leading to special modules in the shell where input files can be selected for simulations with PELMO.

When clicking at one of the two blue boxes simulations can be performed considering the FOCUS groundwater or EFSA soil scenarios. These simulations scenarios will be automatically performed according to the respective recommendations.

The third box can be used to perform individual simulations without the restrictions associated with the predefined scenarios.

PELMO traditionally keeps the input and output files in subfolder of the main directory where the program itself was installed. However, in the new version it is possible to move input and output data to user specific folder. The user has to click at the current project folder and set a new project folder (confirm with RETURN, yellow background colour will disappear, see Figure

10). The shell will copy all input and output files to the new location but also keeps the original information as backup.

3.3 *Creating or modifying pesticide input files*

Pesticide input files can be created or modified when working in the FOCUS, EFSA or user specific part of the shell) by double clicking at the selected pesticide file (see chapter 3.6 and 3.8).

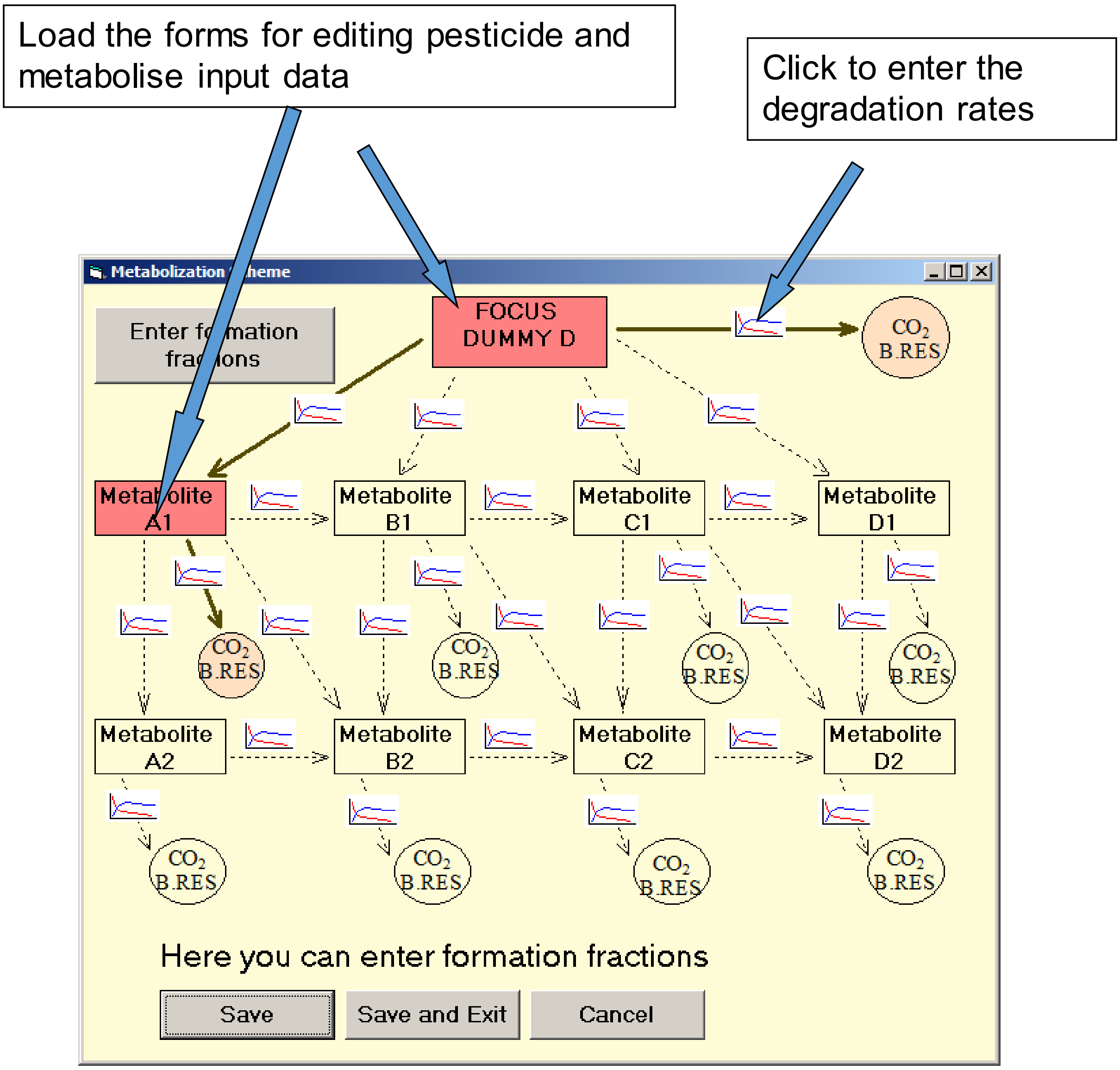
To create pesticide data files for PELMO using WPELMO the user has to follow two steps. First, the metabolism scheme has to be defined. The standard scheme of PELMO is shown in Figure 11.

Compared to the previous versions of PELMO there is a major change with regard to the formation of metabolites reflected by the new button “Enter formation fractions”.

In all previous versions of PELMO the formation of metabolites was expressed based on formation rates (equivalent to degradation of the precursor). If in addition to metabolites also CO_2/bound residues are formed that could be addressed by an extra button. However, this procedure did not match the needs in current procedures in current risk assessment:

The previous procedure in PELMO could only consider formation fractions which were in line with the criteria of conservation of mass. It is however current practice in regulation to use worst case formation fractions for transformation if the experimental formation fraction is not given. For parallel metabolites that could mean that the sum of formation fractions is above 1. Such a scheme could be handled with PELMO only by performing several runs. In the new version the shell was extended and now allows considering formation fractions directly. Also the model had to be extended by adding formation fractions in addition to formation rates. The simulation model internally multiplies the formation fraction with traditional formation rates. The sum of the formation rates still sums up to the total degradation rate of the precursor and the overall degradation date is not affected..

The metabolism scheme shows 9 boxes which represent the parent compound together with 8 transformation products. The boxes can be activated after defining a transformation rate by clicking at the diagrams attached to the dotted arrows. Figure 12 shows the form for metabolites.



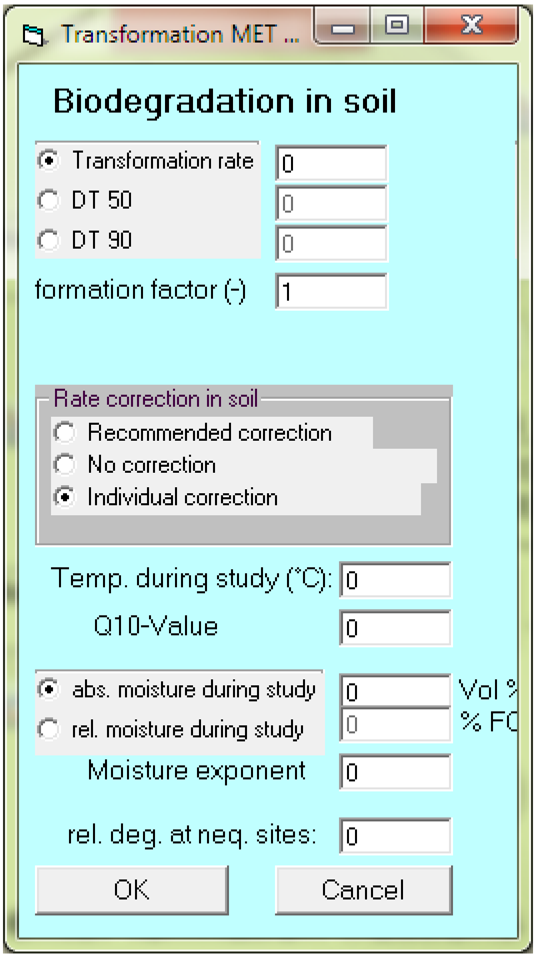
Load the forms for editing pesticide and metabolise input data

Click to enter the degradation rates

Here you can enter formation fractions

Figure 11: PELMO 5.0 metabolism scheme when considering formation rates

The metabolism scheme shows 9 boxes which represent the parent compound together with 8 transformation products. The boxes can be activated after defining a transformation rate by clicking at the diagrams attached to the dotted arrows. Figure 12 shows the form for metabolites.



Biodegradation in soil

● Transformation rate: 0
○ DT 50: 0
○ DT 90: 0
formation factor (-): 1

Rate correction in soil
○ Recommended correction
○ No correction
● Individual correction

Temp. during study (°C): 0
Q10-Value: 0

● abs. moisture during study: 0 Vol
○ rel. moisture during study: 0 % F
Moisture exponent: 0

rel. deg. at neq. sites: 0

Figure 12: PELMO 5.0 Transformation/formation rate form for metabolites

PELMO always considers SFO kinetics which means that the transformation rate can be expressed also by DEGT50 or DEGT90 values. If one of the first three fields is modified, the remaining two will be automatically updated. Then on the form the formation fraction for the respective metabolite can be entered as previously discussed.

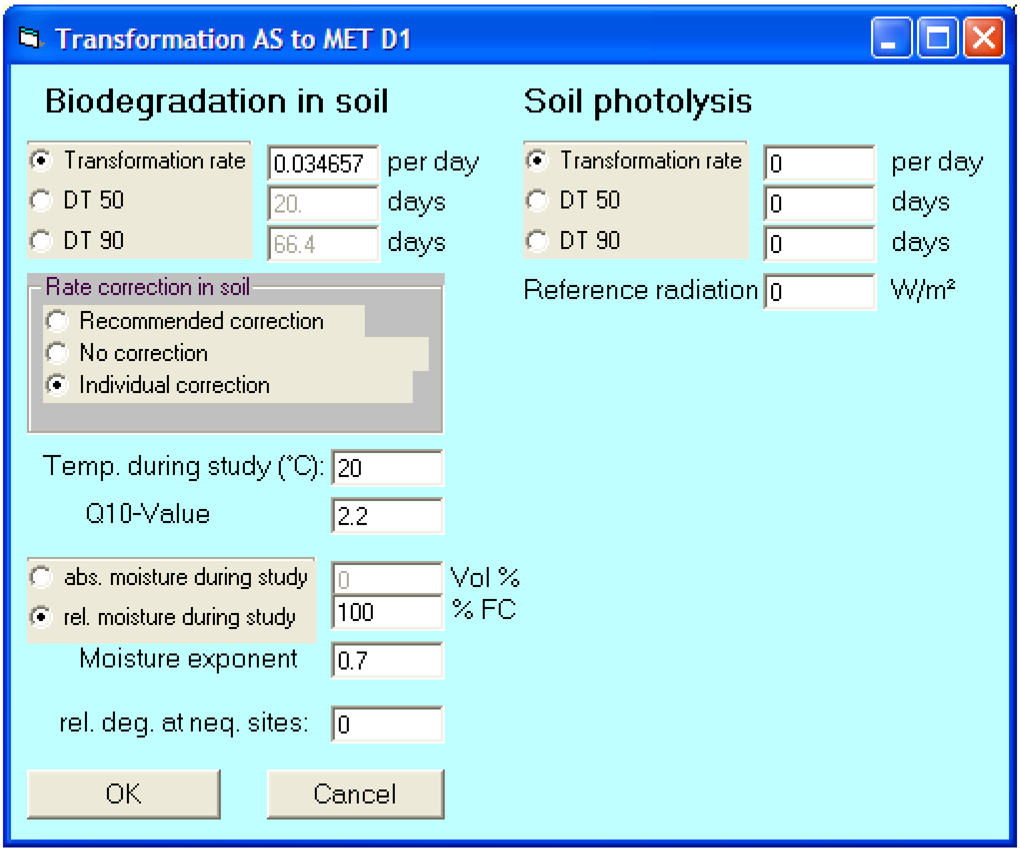
For the temperature and soil moisture correction PELMO offers a “recommended” parameter setting which is suggested by FOCUS (2000) and EFSA (2007) and FOCUS (2009):

- moisture: transformation rate related to field capacity, Walker exponent: 0.7
- temperature: Q10 – factor: 2.58 related to 20 °C.
- relative degradation at non-equilibrium sites set to 0

If a transformation rate other than zero has been entered and the form closed, the black dotted arrow on the metabolism scheme turns into a bold red arrow and the respective red box turns into red.

If a certain transformation pathway should be switched off the respective transformation rate has to be set to “0”.

As an additional transformation process photolysis on the soil surface can be considered when entering a soil photolysis rate together with the references radiation. In addition to microbial degradation the process soil photolysis can be used for the parent to calculate the formation of metabolites. Suitable metabolites in PELMO's scheme are substances Met A1 to Met D1. Therefore, the form shown in Figure 12 was extended for parent compounds as presented in Figure 13.



Transformation AS to MET D1

Biodegradation in soil

● Transformation rate 0.034657 per day
○ DT 50 20. days
○ DT 90 66.4 days

Rate correction in soil
○ Recommended correction
○ No correction
● Individual correction

Temp. during study (°C): 20
Q10-Value 2.2

○ abs. moisture during study 0 Vol %
● rel. moisture during study 100 % FC
Moisture exponent 0.7

rel. deg. at neq. sites: 0

Soil photolysis

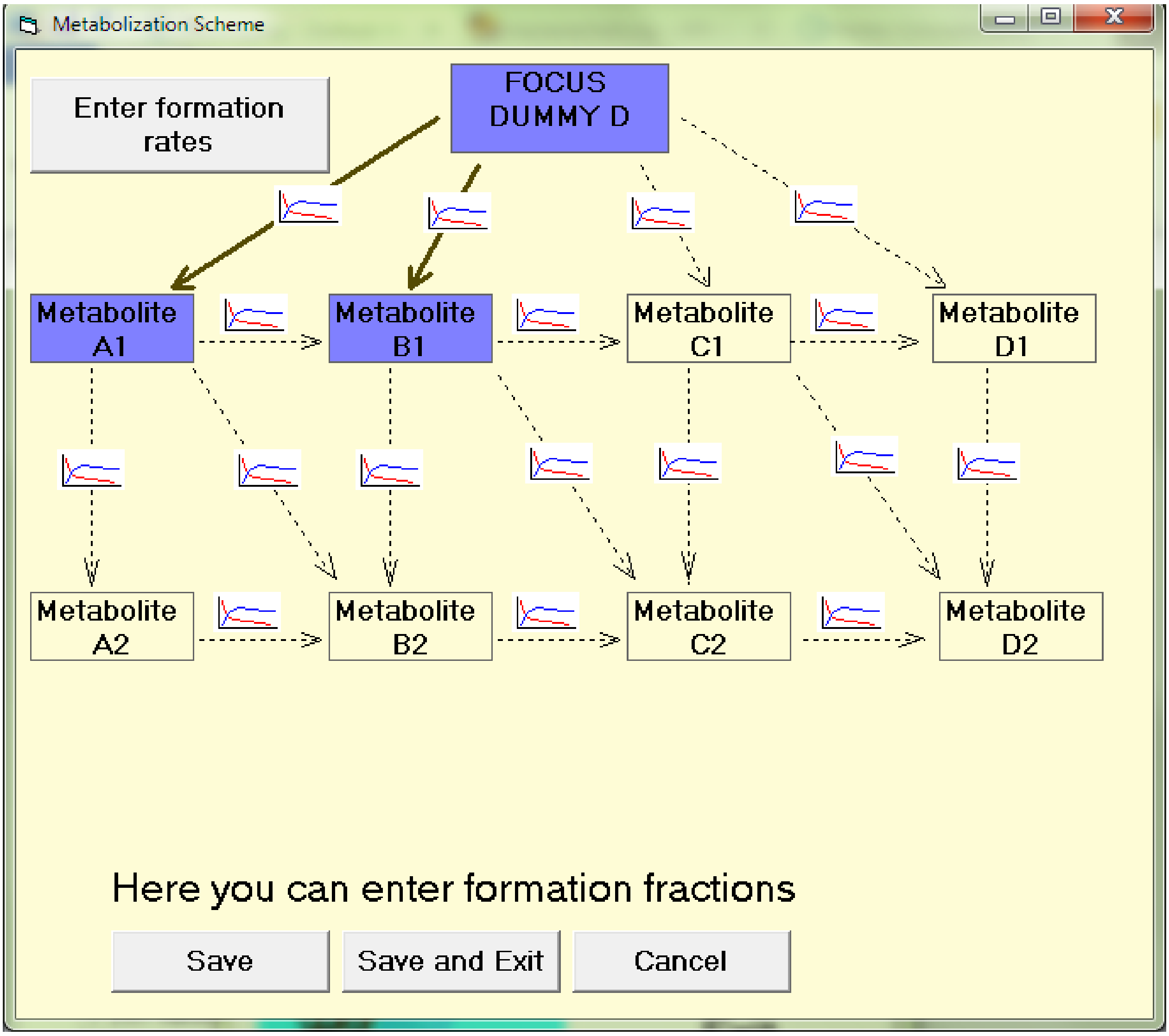
● Transformation rate 0 per day
○ DT 50 0 days
○ DT 90 0 days

Reference radiation 0 W/m²

Figure 13: PELMO 5.0 Transformation rate form for parent

In the second step substance specific input data should be entered for each activated box.

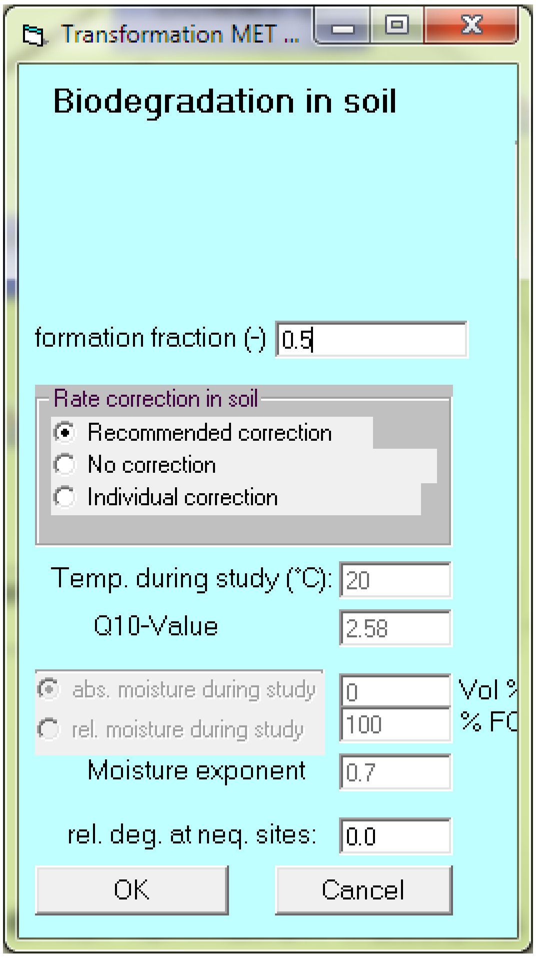
In the new version of PELMO it is up to the user to only enter formation fraction instead of formation rates. The button "Enter formation fraction" on the metabolism scheme will change the form and respective input fields as shown in the next figure.



Here you can enter formation fractions

Figure 14: PELMO 5.0 metabolism scheme when considering formation rates

The main difference compared to the scheme where formation rates can be entered is that all objects that refer to the formation of CO_2/Bound residues have been removed because they are not necessary in this situation.



Biodegradation in soil

formation fraction (-) 0.5

Rate correction in soil
● Recommended correction
○ No correction
○ Individual correction

Temp. during study (°C): 20
Q10-Value 2.58

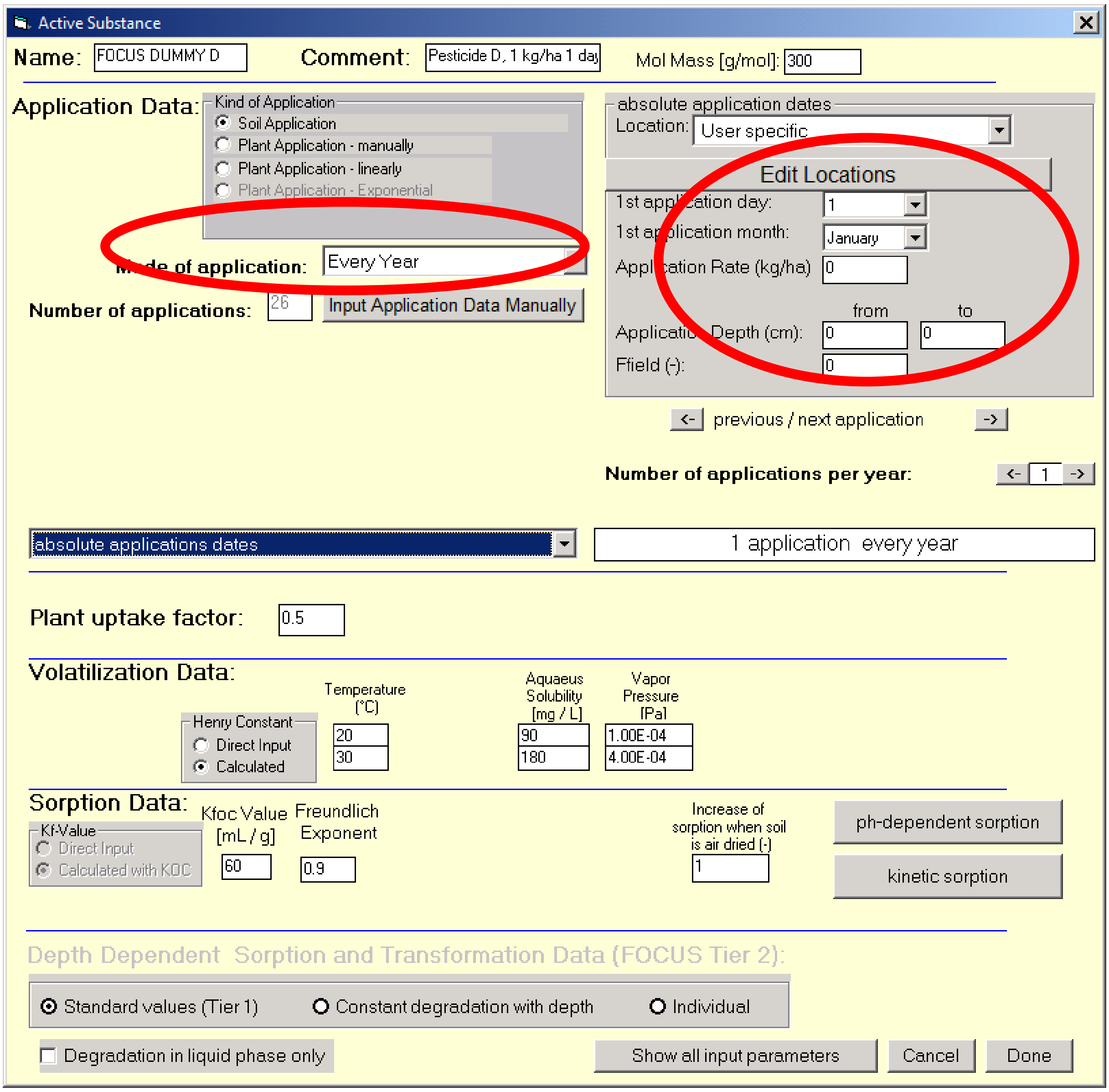
● abs. moisture during study 0 Vol
○ rel. moisture during study 100 % F

Moisture exponent 0.7

rel. deg. at neq. sites: 0.0

Figure 15: PELMO 5.0 formation fraction form for metabolites

The 9 boxes on the form which represent the parent compound together with 8 transformation products can be activated after defining a transformation rate by clicking at the diagrams attached to the dotted arrows. When you click at the parent compound the form shown in Figure 16 appears.



Active Substance

Name: FOCUS DUMMY D
Comment: Pesticide D, 1 kg/ha 1 day
Mol Mass [g/mol]: 300

Application Data:
Kind of Application
● Soil Application
○ Plant Application - manually
○ Plant Application - linearly
○ Plant Application - Exponential
Mode of application: Every Year
Number of applications: 26

absolute application dates
Location: User specific
1st application day: 1
1st application month: January
Application Rate (kg/ha): 0
Application Depth (cm): from 0 to 0
Ffield (-): 0
Number of applications per year: 1

absolute applications dates
1 application every year

Plant uptake factor: 0.5

Volatilization Data:
Henry Constant
○ Direct Input
● Calculated

Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Sorption Data:
Kf-Value
○ Direct Input
● Calculated with KOC
Kfoc Value [mL / g]: 60
Freundlich Exponent: 0.9
Increase of sorption when soil is air dried (-): 1

Depth Dependent Sorption and Transformation Data (FOCUS Tier 2):
● Standard values (Tier 1)
○ Constant degradation with depth
○ Individual

☐ Degradation in liquid phase only

Figure 16: PELMO 5.0 Pesticide input data form (absolute application pattern)

For the application mode the user can decide between absolute applications (application dates related to a certain location independent on the crop) or relative applications (application dates related to a certain crop stage independent on the location).

For absolute application patterns the location must be selected first followed by additional information on the application pattern (application date, rate, depth and Ffield). Location can be added to the compound after clicking at “Edit Locations”

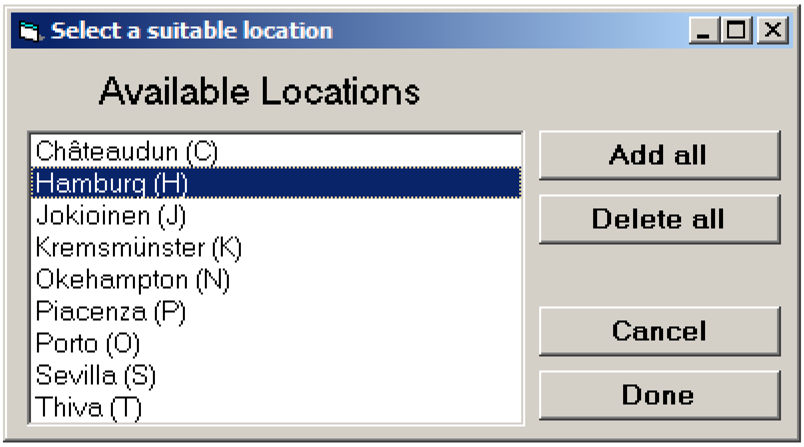
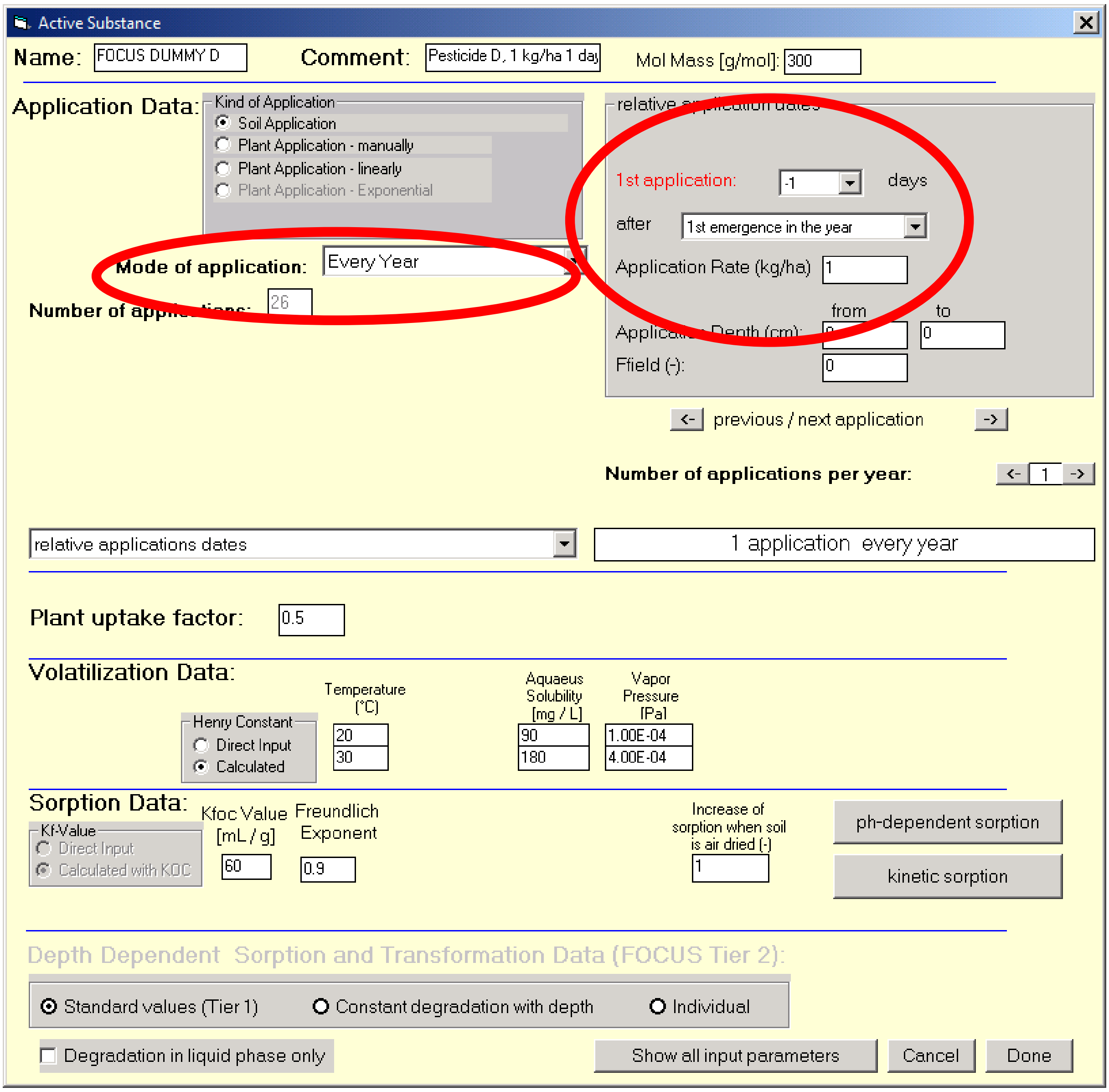


Figure 17: PELMO 5.0 Adding locations to the PSM file (absolute application pattern only)

For each location a different number of applications within a year can be defined. If more than one application per year is to be simulated the total number of application per year must be entered first. Afterwards a certain application within the sequence can be reached by clicking at the arrows “previous/next application”.

In the new versions it is possible to estimate suitable application dates dependent on the location and the crop development (BBCH). The recommendations are based on results of the tool AppDate (Klein 2007). In order to receive a rational application date the user has to enter the crop and the BBCH development stage in the green part of the form. If the recommendation is acceptable it will be automatically transferred into the respective fields on the form. The recommendation is always related to the current location which is selected on the form. The green form will only be enabled if the necessary information is provided in the PELMO subfolder “AppDate”.



Active Substance

Name: FOCUS DUMMY D
Comment: Pesticide D, 1 kg/ha 1 day
Mol Mass [g/mol]: 300

Application Data:
Kind of Application
● Soil Application
○ Plant Application - manually
○ Plant Application - linearly
○ Plant Application - Exponential

Mode of application: Every Year
Number of applications: 26

relative application dates
1st application: -1 days
after 1st emergence in the year
Application Rate (kg/ha) 1
Application Depth (cm): from 0 to 0
Ffield (-): 0

Number of applications per year: 1

relative applications dates
1 application every year

Plant uptake factor: 0.5

Volatilization Data:
Henry Constant
○ Direct Input
● Calculated

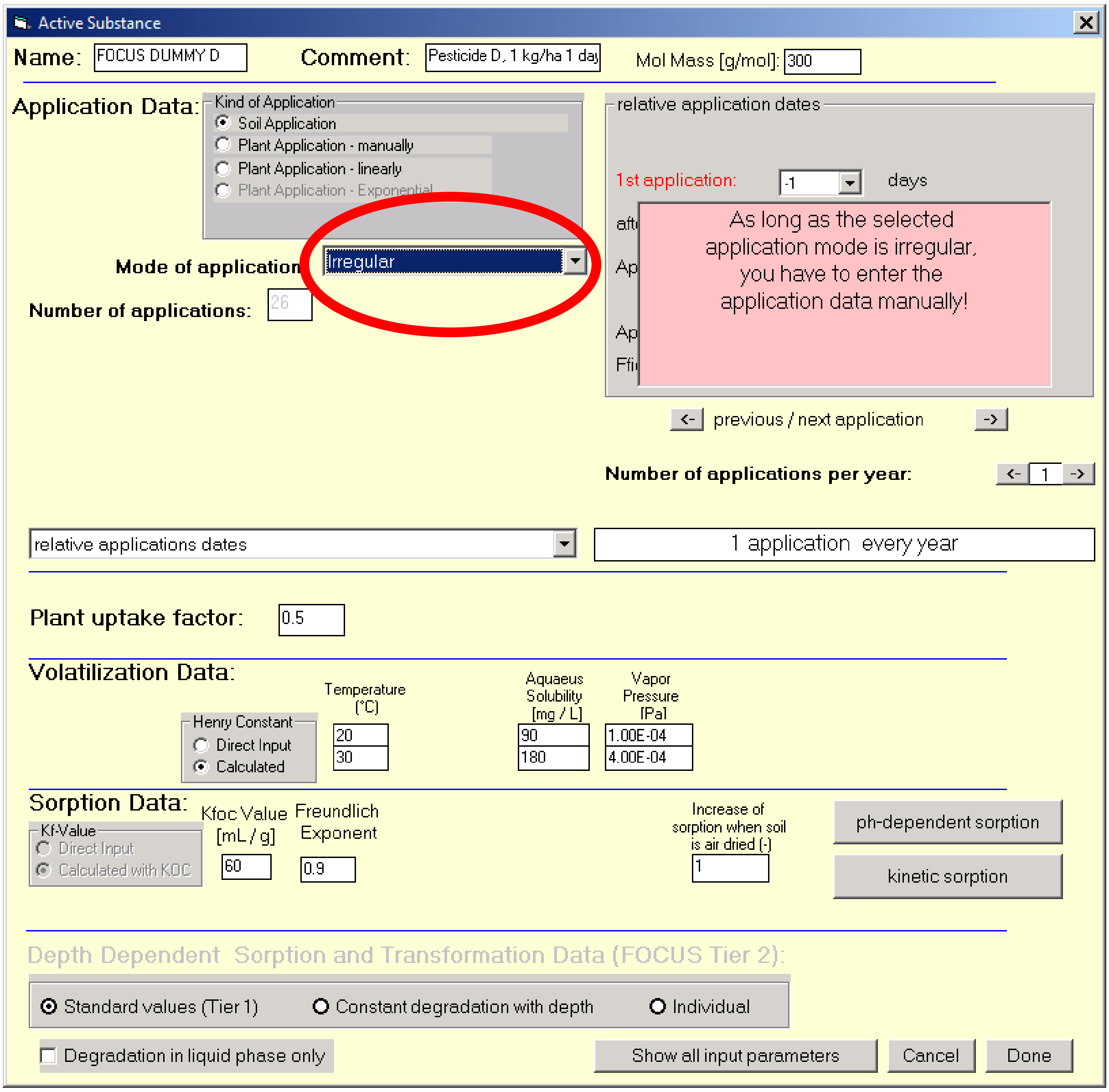
Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Sorption Data:
Kf-Value
○ Direct Input
● Calculated with KOC
Kfoc Value [mL / g]: 60
Freundlich Exponent: 0.9
Increase of sorption when soil is air dried (-): 1

Depth Dependent Sorption and Transformation Data (FOCUS Tier 2):
● Standard values (Tier 1) ○ Constant degradation with depth ○ Individual
☐ Degradation in liquid phase only

Figure 18: PELMO 5.0 pesticide input data form (relative application pattern)

For relative application patterns (Figure 18), the application dates are entered relatively to crop development stages. The crop development stages in the database are based on the FOCUS scheme (FOCUS 2009). If a specific crop is planted more than one time per year (e.g. carrots) the application dates are always related to the first cropping period.
According to the FOCUS recommendations regular applications can be applied annually, biennially, or triennially. Please notice that the entry fields for recommendation of suitable application date is only available if absolute application dates are selected.



Name: FOCUS DUMMY D

Comment: Pesticide D, 1 kg/ha 1 day

Mol Mass [g/mol]: 300

Kind of Application:
● Soil Application
○ Plant Application - manually
○ Plant Application - linearly
○ Plant Application - Exponential

Mode of application: Irregular

Number of applications: 26

1st application: -1 days

As long as the selected application mode is irregular, you have to enter the application data manually!

Number of applications per year: 1

relative applications dates

1 application every year

Plant uptake factor: 0.5

Henry Constant:
○ Direct Input
● Calculated

Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Kf-Value:
○ Direct Input
● Calculated with KOC

Kfoc Value [mL / g]: 60

Freundlich Exponent: 0.9

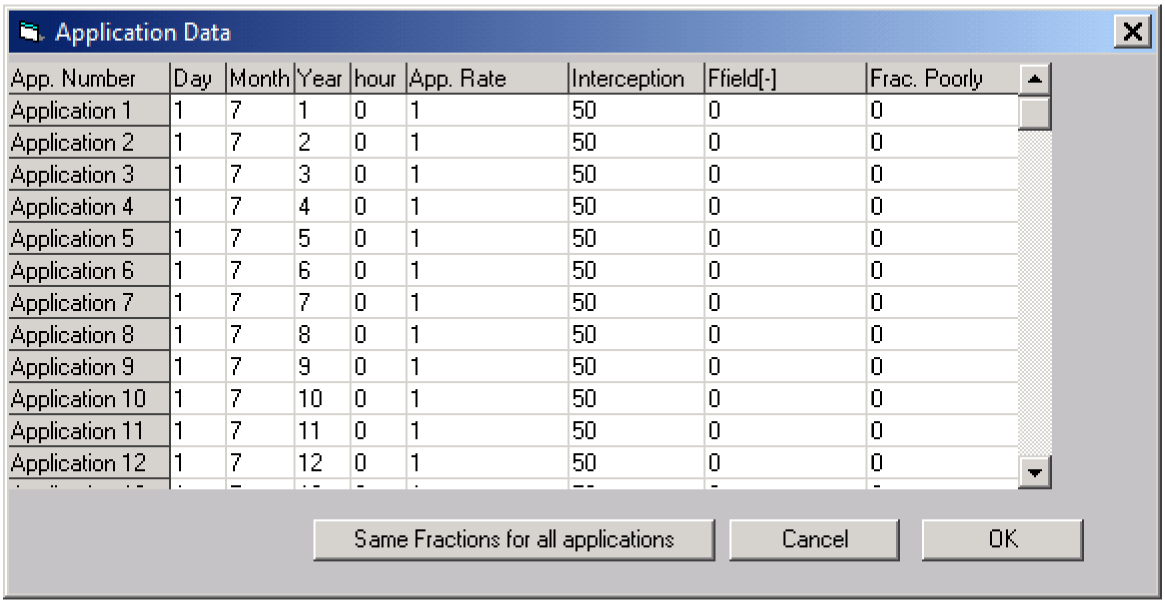
Increase of sorption when soil is air dried (-): 1

● Standard values (Tier 1) ○ Constant degradation with depth ○ Individual

☐ Degradation in liquid phase only

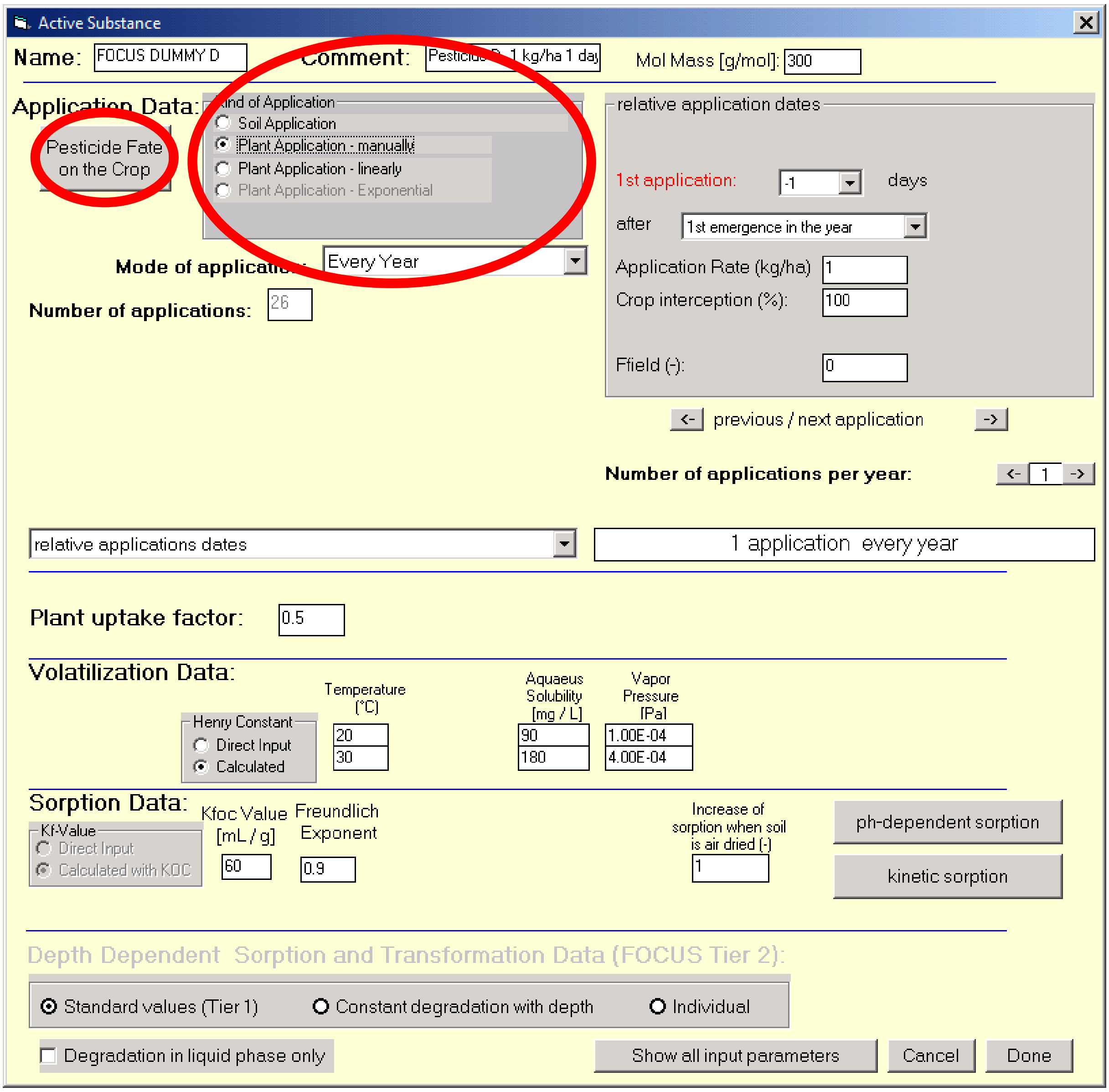
Figure 19: PELMO 5.0 pesticide input data form (irregular application pattern)

If pesticides are applied irregularly (what means that the pattern changes in a different way than described earlier) the application dates must be entered in a specific table which can be called when clicking at the button “Input Application Data Manually” (see Figure 20. In addition to the application date and time this form also allows to enter the poorly exposed pesticide fraction.



App. Number	Day	Month	Year	hour	App. Rate	Interception	Ffield[-]	Frac. Poorly
Application 1	1	7	1	0	1	50	0	0
Application 2	1	7	2	0	1	50	0	0
Application 3	1	7	3	0	1	50	0	0
Application 4	1	7	4	0	1	50	0	0
Application 5	1	7	5	0	1	50	0	0
Application 6	1	7	6	0	1	50	0	0
Application 7	1	7	7	0	1	50	0	0
Application 8	1	7	8	0	1	50	0	0
Application 9	1	7	9	0	1	50	0	0
Application 10	1	7	10	0	1	50	0	0
Application 11	1	7	11	0	1	50	0	0
Application 12	1	7	12	0	1	50	0	0

Figure 20: PELMO 5.0 Input data form for irregular applications



Name: FOCUS DUMMY D

Comment: Pesticide D 1 kg/ha 1 day

Mol Mass [g/mol]: 300

Application Data:

Kind of Application
○ Soil Application
● Plant Application - manually
○ Plant Application - linearly
○ Plant Application - Exponential

Mode of application: Every Year

Number of applications: 26

relative application dates

1st application: -1 days

after 1st emergence in the year

Application Rate (kg/ha) 1

Crop interception (%): 100

Ffield (-): 0

Number of applications per year: 1

relative applications dates

1 application every year

Plant uptake factor: 0.5

Volatilization Data:

Henry Constant
○ Direct Input
● Calculated

Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Sorption Data:

Kf-Value
○ Direct Input
● Calculated with KOC

Kfoc Value [mL / g]: 60

Freundlich Exponent: 0.9

Increase of sorption when soil is air dried (-): 1

Depth Dependent Sorption and Transformation Data (FOCUS Tier 2):

● Standard values (Tier 1) ○ Constant degradation with depth ○ Individual

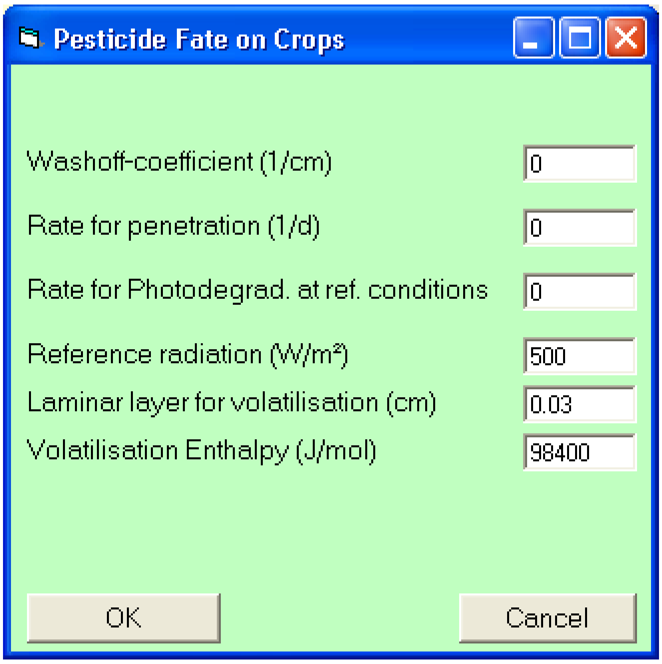
☐ Degradation in liquid phase only

Figure 21: PELMO 5.0 Pesticide input data form (Soil or plant application)

PELMO distinguishes between four different kinds of application

- soil application (which is the default for FOCUS groundwater simulations)
- plant application – manual crop interception
- plant application - linear model
- plant application - exponential model

“plant application – manual crop interception” is an option which allows the definition of a percentile of the rate which remains on the crop but maybe reaches the soil later due to wash-off induced by rainfall and irrigation. The other two options define the crop interception automatically according to the actual development of the crop. The pesticide fate on plant surfaces can be described in a new form which is loaded after clicking at the button “pesticide fate on the crop” (see Figure 19).

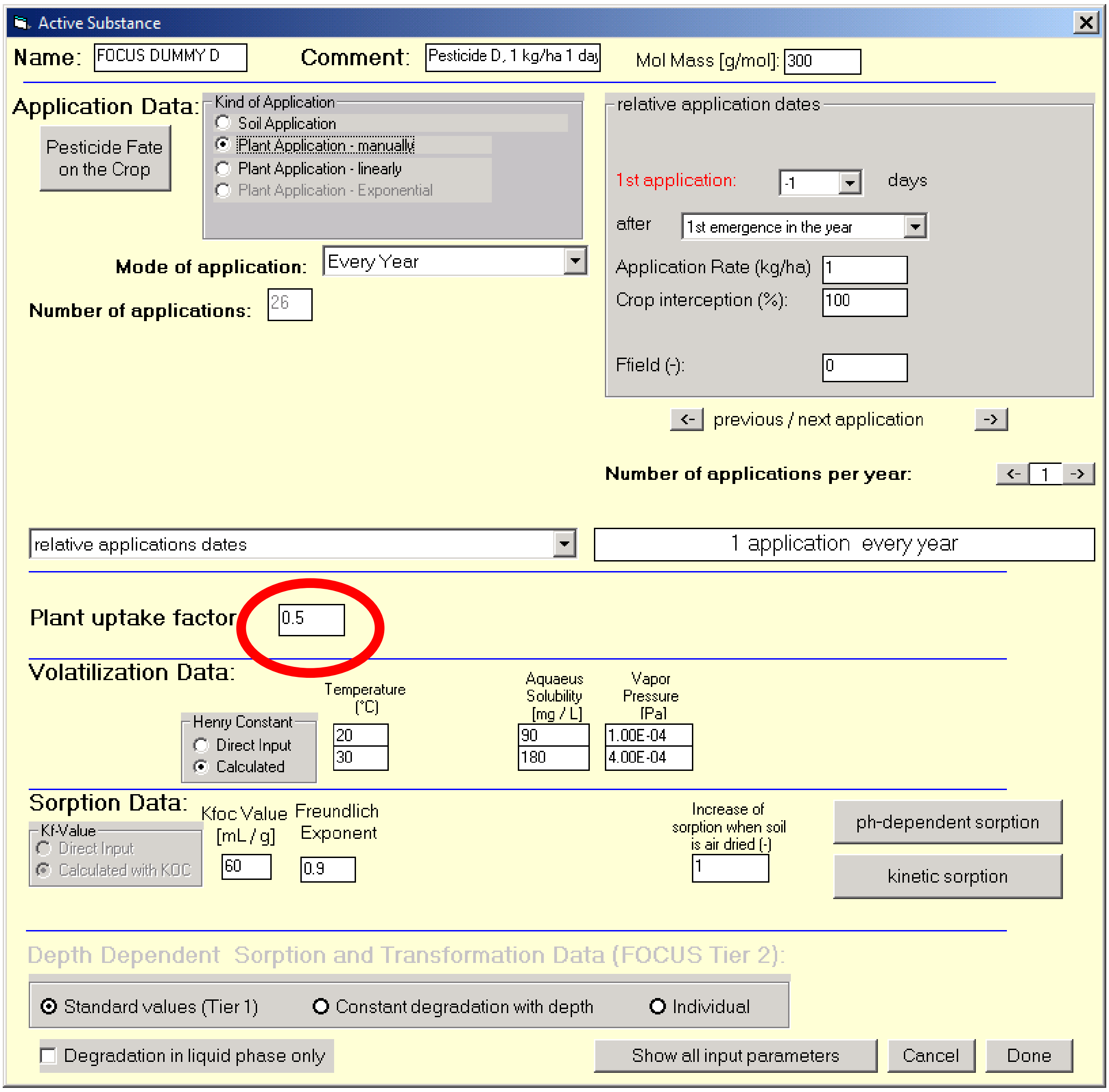


Washoff-coefficient (1/cm) 0
Rate for penetration (1/d) 0
Rate for Photodegrad. at ref. conditions 0
Reference radiation (W/m²) 500
Laminar layer for volatilisation (cm) 0.03
Volatilisation Enthalpy (J/mol) 98400

Figure 22: PELMO 5.0 Pesticide fate on the crop surface

Four different processes (wash-off from plants, penetration into plants, volatilisation from plants, photo-degradation on plants) can be simulated if the necessary input parameters are entered. If a certain process should be switched off, the respective rate constant has to be set to “0”.

PELMO considers the uptake of pesticides by plant roots (see Figure 23). The recommended value for systemic compounds is “0.5” which means that the pesticide concentration in the water taken up by the plant root is 50 % of the pore water concentration in the respective soil layer.
If the parameter is set to “0” pesticide uptake by plant roots will be switched off.



Active Substance

Name: FOCUS DUMMY D

Comment: Pesticide D, 1 kg/ha 1 day

Mol Mass [g/mol]: 300

Application Data:

Kind of Application

○ Soil Application

● Plant Application - manually

○ Plant Application - linearly

○ Plant Application - Exponential

Mode of application: Every Year

Number of applications: 26

relative application dates

1st application: -1 days

after 1st emergence in the year

Application Rate (kg/ha) 1

Crop interception (%): 100

Ffield (-): 0

Number of applications per year: 1

relative applications dates

1 application every year

Plant uptake factor 0.5

Volatilization Data:

Henry Constant

○ Direct Input

● Calculated

Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Sorption Data:

Kf-Value

○ Direct Input

● Calculated with KOC

Kfoc Value [mL / g]: 60

Freundlich Exponent: 0.9

Increase of sorption when soil is air dried (-): 1

Depth Dependent Sorption and Transformation Data (FOCUS Tier 2):

● Standard values (Tier 1) ○ Constant degradation with depth ○ Individual

☐ Degradation in liquid phase only

Figure 23: PELMO 5.0 Modifying the plant root uptake factor

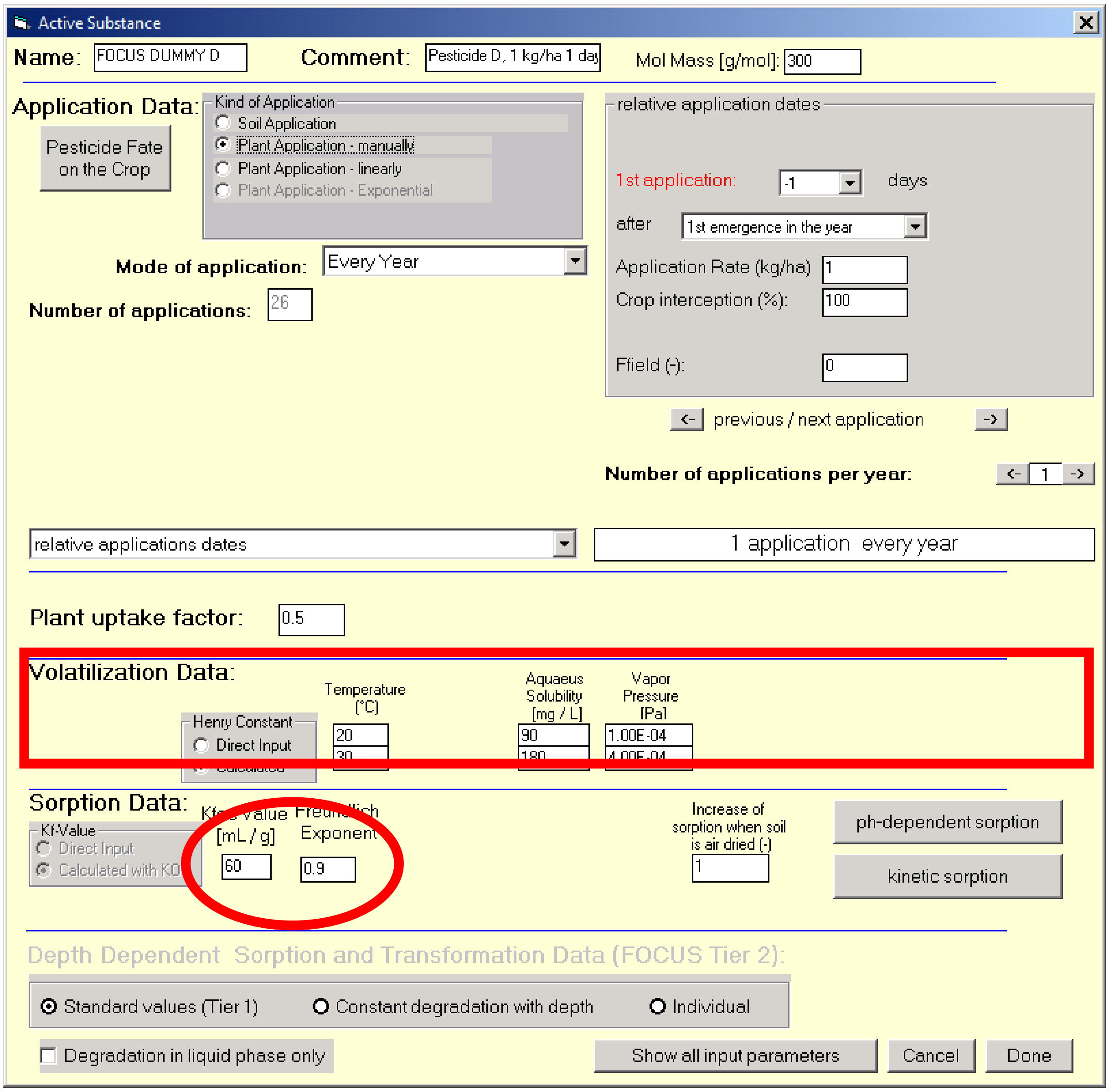
For the estimation of temperature dependent volatilisation from soil surfaces and the transport in the soil air Henry's law constant (or alternatively: water solubility and vapour pressure) must be given for 2 different temperatures (see the rectangle in Figure 24).

If these parameters are only known at one single temperature the following procedure is recommended:

The additional temperature is defined 10 °C higher than the original temperature.

The 2nd Henry's law constant or the 2nd water solubility is defined two times the original values.

The 2nd vapour pressure is defined 4 times the original vapour pressure.



Active Substance

Name: FOCUS DUMMY D

Comment: Pesticide D, 1 kg/ha 1 day

Mol Mass [g/mol]: 300

Application Data:

Kind of Application
○ Soil Application
● Plant Application - manually
○ Plant Application - linearly
○ Plant Application - Exponential

Mode of application: Every Year

Number of applications: 26

relative application dates

1st application: -1 days

after 1st emergence in the year

Application Rate (kg/ha) 1

Crop interception (%): 100

Ffield (-): 0

Number of applications per year: 1

relative applications dates

1 application every year

Plant uptake factor: 0.5

Volatilization Data:

Henry Constant
○ Direct Input
● Calculated

Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Sorption Data:

Kf-Value
○ Direct Input
● Calculated with KOC

Kfoc-value [mL / g]: 60

Freundlich Exponent: 0.9

Increase of sorption when soil is air dried (-): 1

Depth Dependent Sorption and Transformation Data (FOCUS Tier 2):

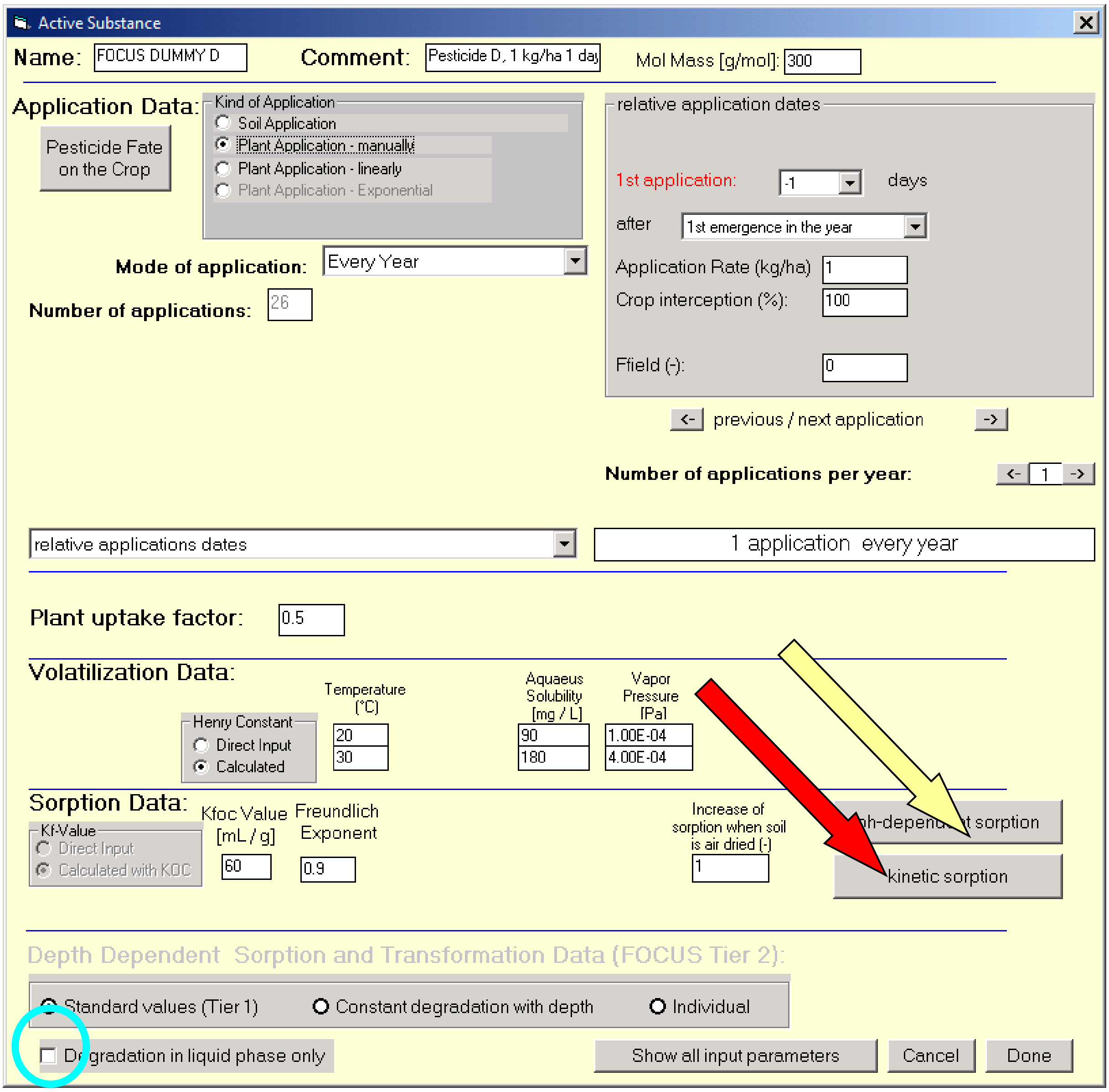
● Standard values (Tier 1) ○ Constant degradation with depth ○ Individual

☐ Degradation in liquid phase only

Figure 24: PELMO 5.0 Considering volatilisation

The simplest way to consider sorption is to enter Kfoc-value and the respective Freundlich exponent. If necessary, depth dependent Kf-values, kinetic sorption parameters or pH-dependent sorption in soil can be considered on additional forms which can be called by clicking at the respective buttons (see the arrows in Figure 25).

In the new version degradation in soil can be restricted to the soil water phase by clicking at the check box (see the blue circle in Figure 25.



Name: FOCUS DUMMY D

Comment: Pesticide D, 1 kg/ha 1 day

Mol Mass [g/mol]: 300

Application Data:

Kind of Application

○ Soil Application

● Plant Application - manually

○ Plant Application - linearly

○ Plant Application - Exponential

Mode of application: Every Year

Number of applications: 26

relative application dates

1st application: -1 days

after 1st emergence in the year

Application Rate (kg/ha) 1

Crop interception (%): 100

Ffield (-): 0

Number of applications per year: 1

relative applications dates

1 application every year

Plant uptake factor: 0.5

Volatilization Data:

Henry Constant

○ Direct Input

● Calculated

Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

Sorption Data:

Kf-Value

○ Direct Input

● Calculated with KOC

Kfoc Value [mL / g]: 60

Freundlich Exponent: 0.9

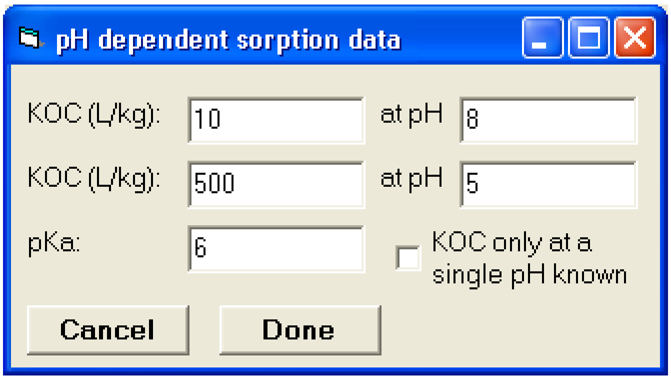
Increase of sorption when soil is air dried (-): 1

Depth Dependent Sorption and Transformation Data (FOCUS Tier 2):

○ Standard values (Tier 1) ○ Constant degradation with depth ○ Individual

☐ Degradation in liquid phase only

Figure 25: PELMO 5.0 Extended Input sheet to consider kinetic sorption in PELMO



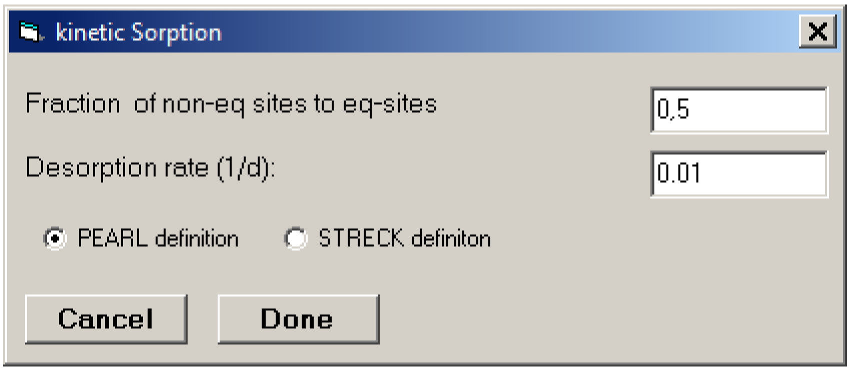
KOC (L/kg): 10 at pH 8

KOC (L/kg): 500 at pH 5

pKa: 6

☐ KOC only at a single pH known

Figure 26: PELMO 5.0 pH-dependent sorption form



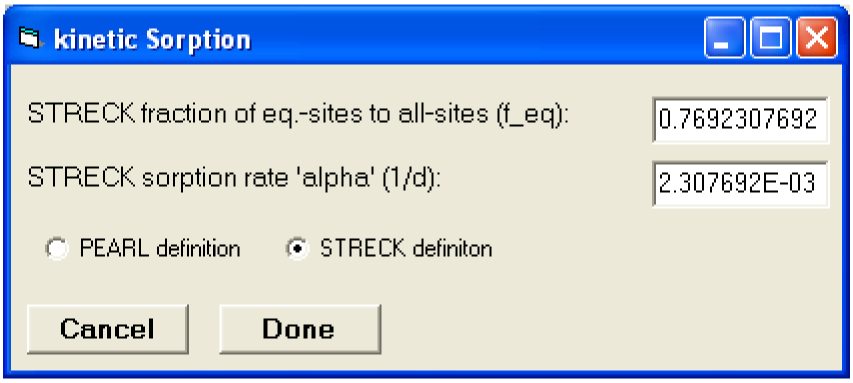
Fraction of non-eq sites to eq-sites: 0.5

Desorption rate (1/d): 0.01

● PEARL definition ○ STRECK definiton

Figure 27: PELMO 5.0 Kinetic sorption form

The forms for pH-dependent sorption and kinetic sorption parameterisation are presented in Figure 26 and Figure 27, respectively. If pesticide input files include parameters for the estimation of these processes flags appear on the main pesticide input form (see Figure 24).
It is possible to select PEARL or Streck parameter definitions (see FOCUS, 2009) by using the radio buttons on the form. Figure 27 shows the PEARL input parameters, Figure 28 the respective Streck variables. When switching between the two modes the parameters are automatically transferred according to the equations in the previous chapter.
When using the non-equilibrium sorption module in PELMO it has to be considered that - compared to the traditional definition of the sorption constant in PELMO - the Streck definition is different because it is related to the equilibrium domain in soil only and not (as in previous PELMO versions) to the total soil (equilibrium and non-equilibrium domain). That may lead to confusion when kinetic sorption is switched off (desorption rate set to “0”). Still overall sorption constants will depend on f_{eq} (Streck). Therefore, in the field “Kfoc Value” (see the yellow arrow in Figure 25) always the equilibrium sorption constant related to the whole soil has to be entered (consistent with previous versions of PELMO).



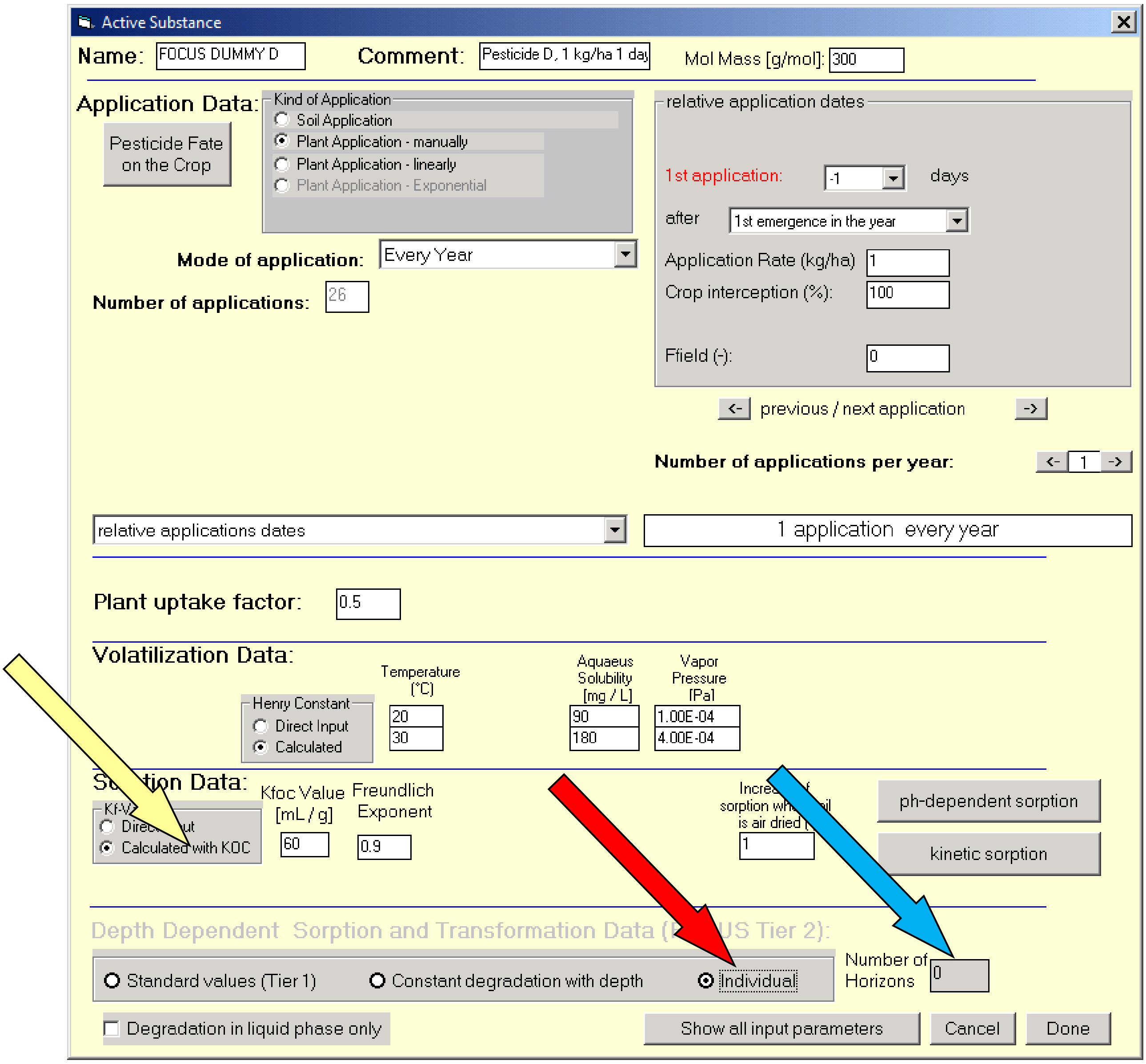
STRECK fraction of eq.-sites to all-sites (f_eq): 0.7692307692

STRECK sorption rate 'alpha' (1/d): 2.307692E-03

○ PEARL definition ● STRECK definiton

Figure 28: Parameter setting using the Streck-model

The user can select Kf-values individually for each compound. For this option, depth dependent sorption and transformation data has to be set to “individual” (see Figure 29, red arrow). If the sorption of the active substance should be calculated based on Kf-values (not correlated to OC), the user has to switch the “Direct input” for Kf-values (see the yellow arrow in Figure 29).



Name: FOCUS DUMMY D
Comment: Pesticide D, 1 kg/ha 1 day
Mol Mass [g/mol]: 300

Application Data:
Kind of Application
○ Soil Application
● Plant Application - manually
○ Plant Application - linearly
○ Plant Application - Exponential

Mode of application: Every Year
Number of applications: 26

relative application dates
1st application: -1 days
after 1st emergence in the year
Application Rate (kg/ha) 1
Crop interception (%): 100
Ffield (-): 0

Number of applications per year: 1

relative applications dates
1 application every year

Plant uptake factor: 0.5

Volatilization Data:
Henry Constant
○ Direct Input
● Calculated

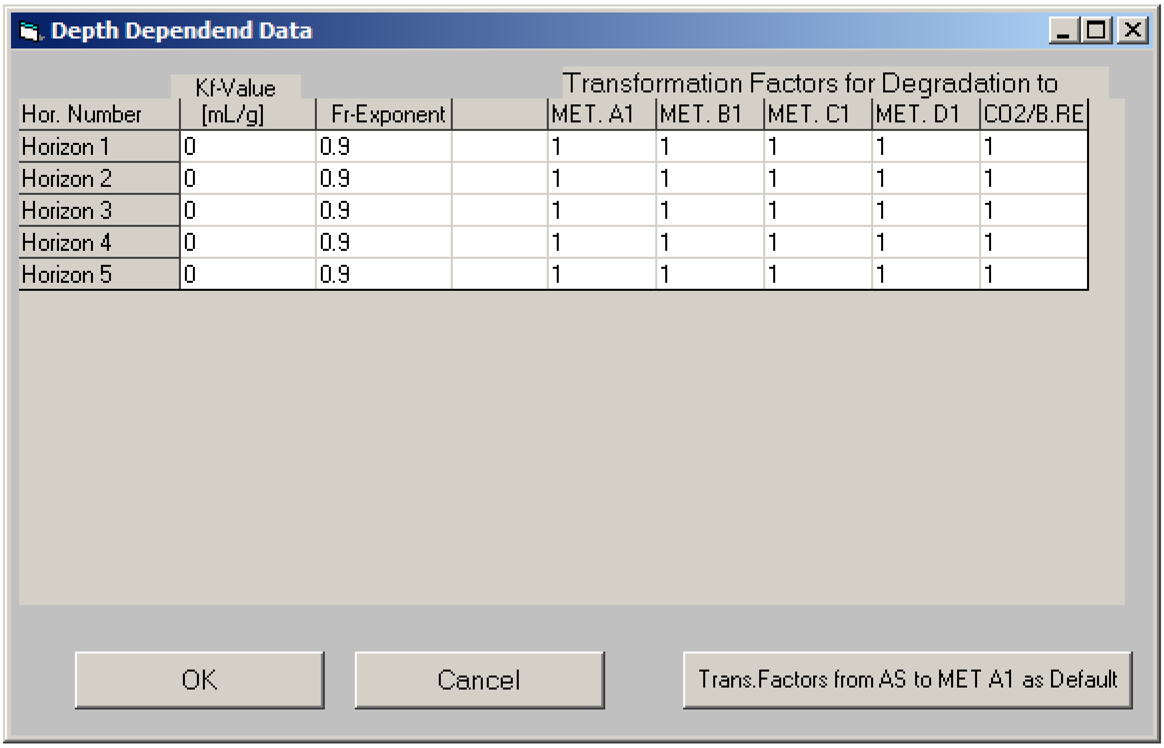
Temperature [°C]	Aquaeus Solubility [mg / L]	Vapor Pressure [Pa]
20	90	1.00E-04
30	180	4.00E-04

So tion Data:
Kf-V
○ Direc ut
● Calculated with KOC
Kfoc Value [mL / g] 60
Freundlich Exponent 0.9
Incre f sorption wh il is air dried 1

Depth Dependent Sorption and Transformation Data (US Tier 2):
○ Standard values (Tier 1)
○ Constant degradation with depth
● Individual
Number of Horizons 0
☐ Degradation in liquid phase only

Figure 29: PELMO 5.0 Extended Input form to consider kinetic sorption in PELMO

To enter the Kf-values the number of horizons for -Kkf-values has to be set. This number should be defined according to the number of horizons in the soil file. As soon as a number >0 is entered an additional button appears on the form “Edit numbers” which calls a new form where the Kf-values can be entered (see Figure 30).



Hor. Number	Kf-Value [mL/g]	Fr-Exponent		MET. A1	MET. B1	MET. C1	MET. D1	CO2/B.RE
Horizon 1	0	0.9		1	1	1	1	1
Horizon 2	0	0.9		1	1	1	1	1
Horizon 3	0	0.9		1	1	1	1	1
Horizon 4	0	0.9		1	1	1	1	1
Horizon 5	0	0.9		1	1	1	1	1

Transformation Factors for Degradation to

Figure 30: PELMO 5.0 Editing individual Kf-values, Freundlich exponents and depth degradation factors

Unfortunately for these type of simulations you also have to set the depth transformation factors for biodegradation manually. The information per horizon is shown in the table below for the different FOCUS groundwater locations.

Table 4: Depth degradation factors for the FOCUS groundwater locations

Scenario	Châteaudun	Hamburg	Jokioinen	Kremsmünster	Okehampton	Piacenza	Porto	Sevilla
Horizons	7	6	6	5	5	6	4	6
	Transformation factors for degradation (per horizon)							
1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0
3	0.5	0.3	0.3	0.5	0.3	0.5	0.3	0.5
4	0.3	0.3	0.3	0.3	0.3	0.3	0	0.3
5	0	0.3	0	0	0	0.3		0
6	0	0	0			0		0
7	0							

3.4 Creating or modifying soil data files

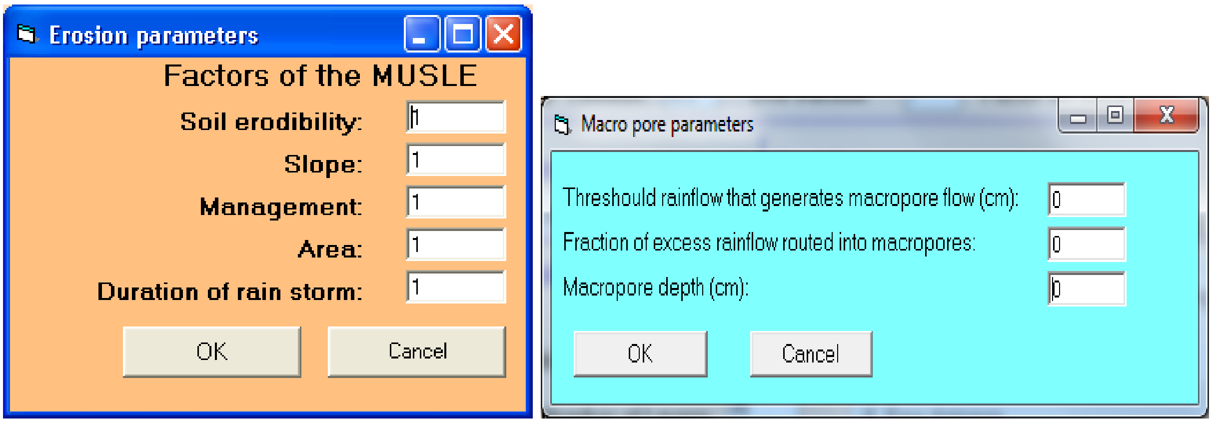
When doing FOCUS groundwater or EFSA soil simulations the user should not change the soil profile information.

Nevertheless soil input files can be created either by double clicking at the respective soil input file at the FOCUS or user specific part of the shell.

3.4.1 Fast processes (run-off, soil erosion, macro pore flow)

If fast processes like run-off, soil erosion or macro pore flow should be considered in simulations first the processes have to be activated by clicking at the respective check boxes (see the arrow in Figure 32). If the boxes are checked the input field for entering the depth which is field up to field capacity before the run-off events begins (“run-off depth”) becomes visible. Further run-off parameters are available under crop rotation on this form.

The additional parameters for soil erosion and macro pore flow are summarised on separate forms which are accessible via special buttons on the form.



Factors of the MUSLE

Soil erodibility: 1

Slope: 1

Management: 1

Area: 1

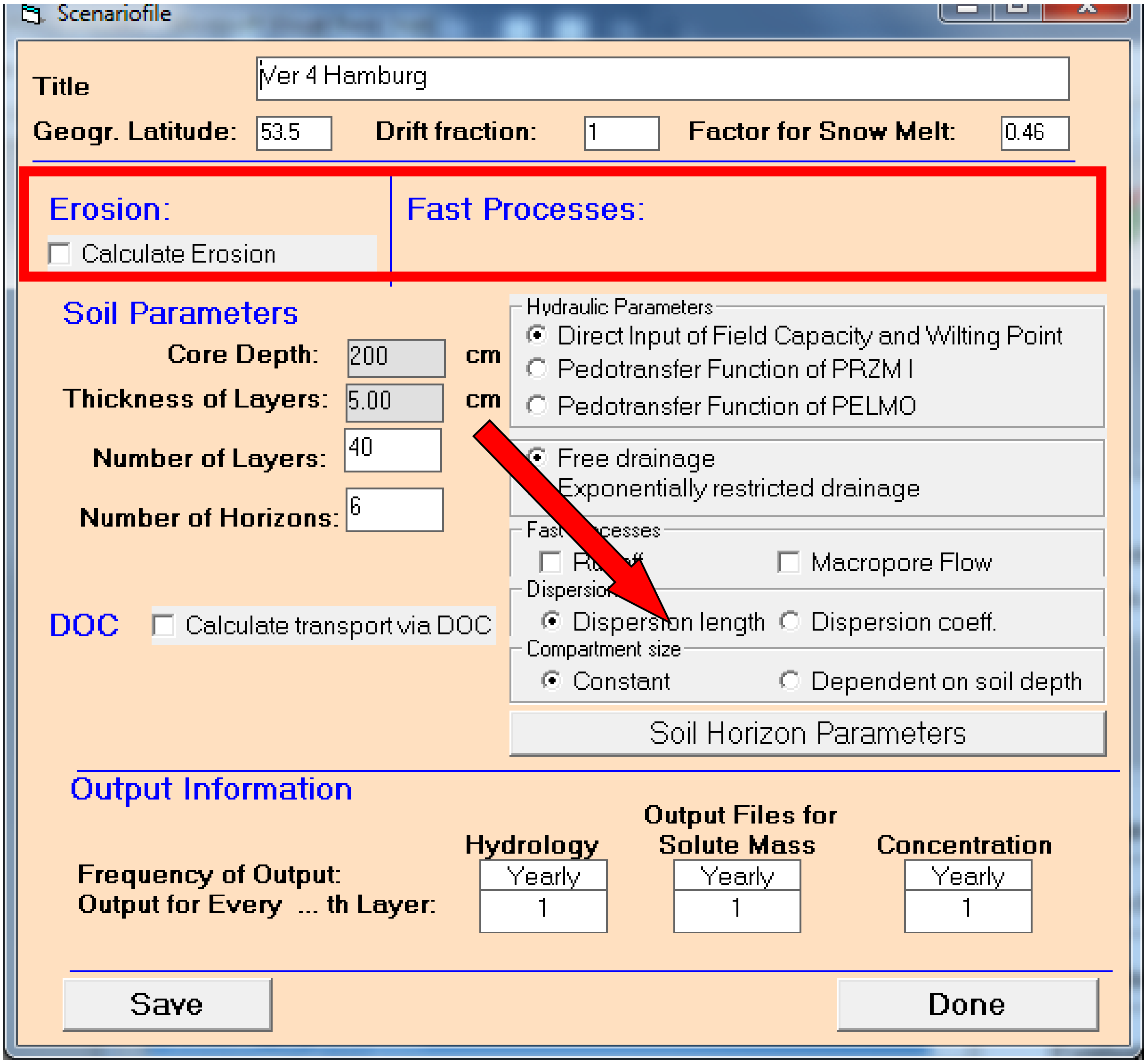
Duration of rain storm: 1

Threshould rainflow that generates macropore flow (cm): 0

Fraction of excess rainflow routed into macropores: 0

Macropore depth (cm): 0

Figure 31: PELMO 5.0 Soil input form: soil erosion and macro pore flow



Title: Ver 4 Hamburg

Geogr. Latitude: 53.5 Drift fraction: 1 Factor for Snow Melt: 0.46

Erosion:

☐ Calculate Erosion

Fast Processes:

Soil Parameters

Core Depth: 200 cm

Thickness of Layers: 5.00 cm

Number of Layers: 40

Number of Horizons: 6

DOC ☐ Calculate transport via DOC

Hydraulic Parameters

● Direct Input of Field Capacity and Wilting Point

○ Pedotransfer Function of PRZM I

○ Pedotransfer Function of PELMO

● Free drainage

○ Exponentially restricted drainage

Fast Processes

☐ Runoff ☐ Macropore Flow

Dispersion

● Dispersion length ○ Dispersion coeff.

Compartment size

● Constant ○ Dependent on soil depth

Output Information

	Hydrology	Solute Mass	Concentration
		Output Files for	
Frequency of Output:	Yearly	Yearly	Yearly
Output for Every ... th Layer:	1	1	1

Figure 32: PELMO 5.0 Soil input form: Fast processes

Only limited experience have been made with the macro pore flow component. Based on the results of the APECOP project (Vanclooster et al. 2003b) it is recommended to calibrate the macro pore flow routine. Meaningful setting for the additional parameter are when starting with the calibration could be 0.5 mm to 1.0 mm for the threshold rainfall, 0.25 to 0.5 for the rainflow fraction that routes into macro pores, and 70 to 90 cm for the length of the macro pores (Kördel et al. 2003, Vanclooster et al. 2007) . If the DOC box is checked and a value for the OC complex formation constant is given in the pesticide input form an additional transport in soil water via complexation to DOC is simulated.

3.4.2 Soil profile information

As mentioned earlier soil properties are defined for each soil horizon. To mimic the gradient of pesticide concentrations in the soil core each soil horizon is divided into a number of layers. It is assumed that all soil profile parameters (e.g. pH value, organic carbon content) data are constant within a horizon.

Before the properties of the soil core can be defined first the number of layers have to be set, either manually ("*constant"*) or automatically by the model ("*dependent on soil depth*"). Dependent on that selection the input form for the number of compartments (red rectangle Figure 33) is adapted. "*Dependent on soil depth*" will define the compartment size dependent on the depth dependent biodegradation factor according to following table:

Table 5: Compartment size dependent on biodegradation

biodegradation factor k_{bio}r	compartment size (cm)
>0.5	1
<0.5, but >0.3	2.5
<=0.3	5

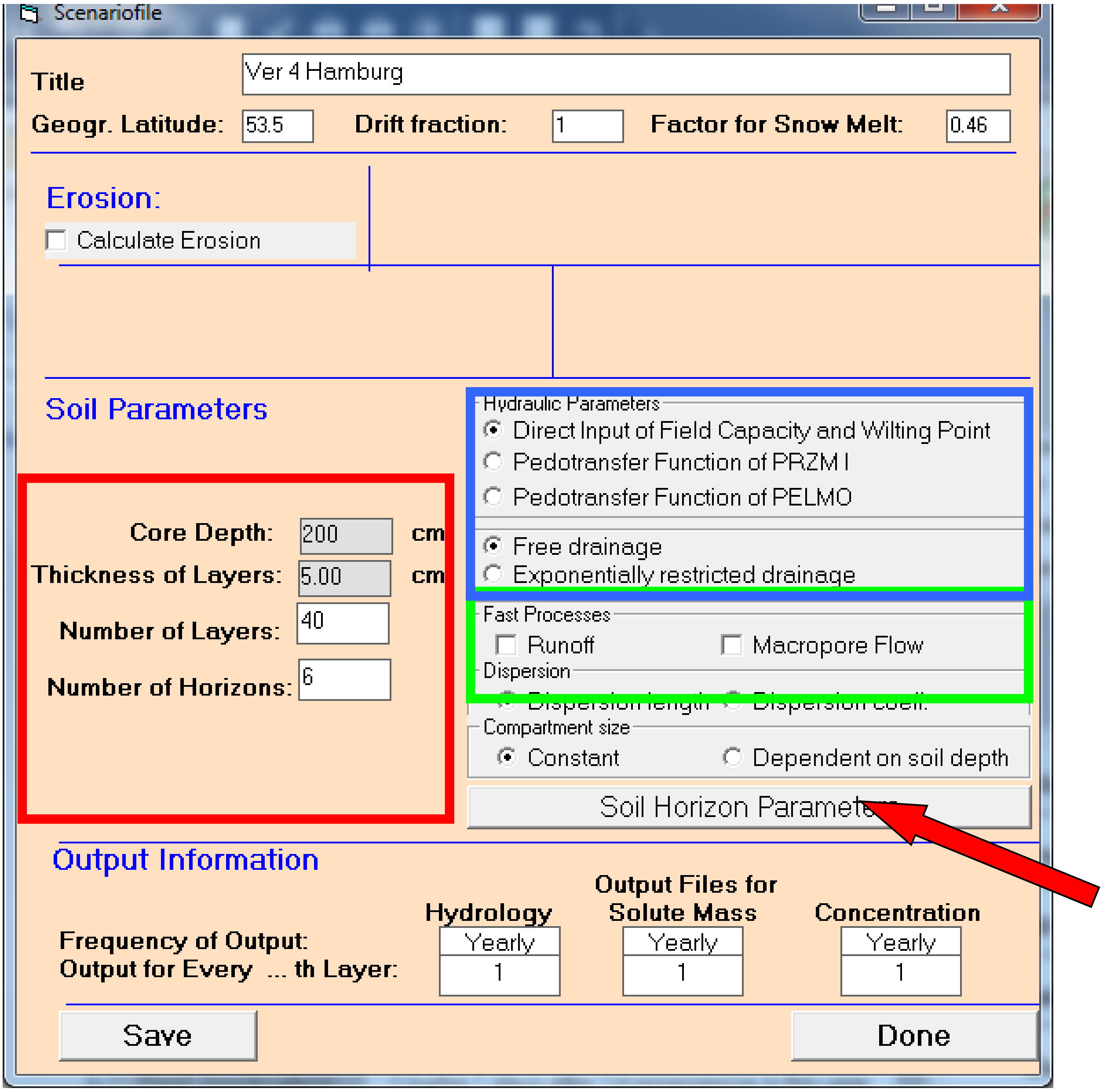
Only a single parameter is left in the red rectangle (Figure 33), if "*Dependent on soil depth*" has been selected, namely the number of soil horizons.

If the compartment size should be entered manually ("constant compartment size") the number of compartments has to be additionally entered in the red rectangle (Figure 33).

PELMO is able to process either dispersion coefficients or dispersion lengths when considering dispersion in soil. In the green rectangle (Figure 33) the user selects his preference. Dependent on that selection the input form for the soil profile information is adapted accordingly (Figure 34).

The parameters highlighted in the blue rectangle (Figure 33) are to specify whether the key soil profile parameters field capacity and wilting point given directly ore by using two different pedo-transfer functions (see section 2.3.8.1). Dependent on that selection the input form for the soil profile information is adapted accordingly (Figure 34). The drainage options “free drainage” or “exponentially restricted drainage” refer to the calculation of soil moisture explained in section 2.3.8.1.

The default option is “free drainage” which means that field soils reach field capacity after a rainfall event after one day. The second option is provided to simulate soils with low permeability layers that restrict the drainage.



Title Ver 4 Hamburg

Geogr. Latitude: 53.5 **Drift fraction:** 1 **Factor for Snow Melt:** 0.46

☐ Calculate Erosion

Core Depth: 200 cm

Thickness of Layers: 5.00 cm

Number of Layers: 40

Number of Horizons: 6

● Direct Input of Field Capacity and Wilting Point
○ Pedotransfer Function of PRZM I
○ Pedotransfer Function of PELMO

● Free drainage
○ Exponentially restricted drainage

☐ Runoff ☐ Macropore Flow

○ Dispersion length ○ Dispersion coeff.

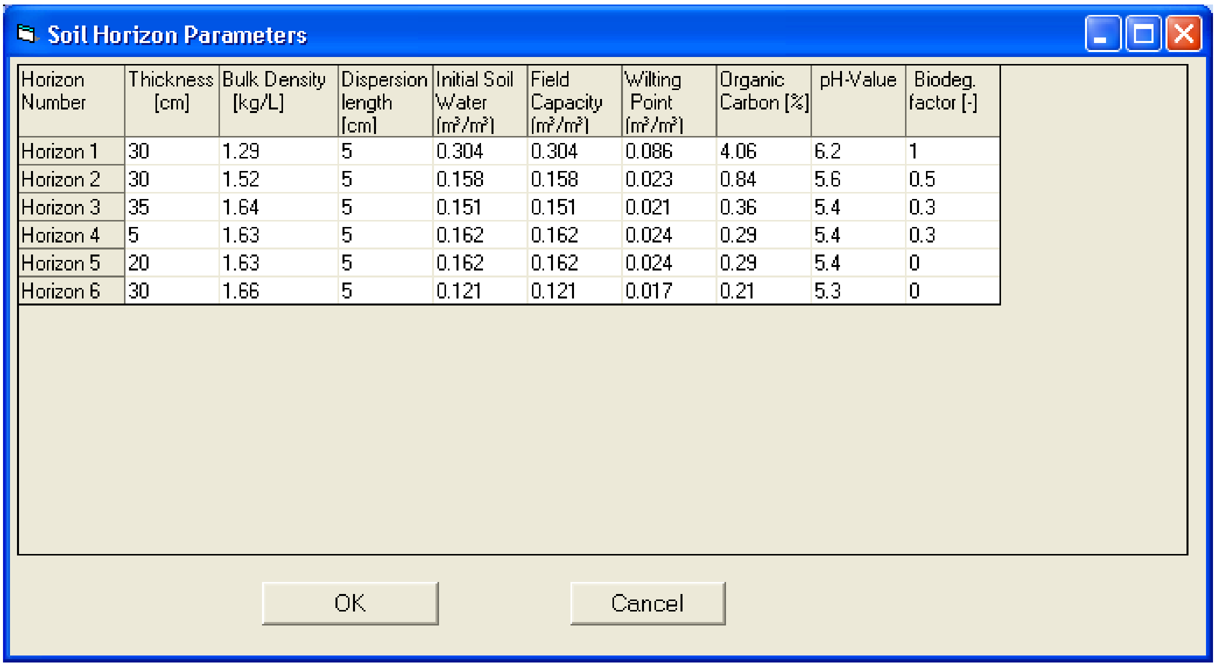
● Constant ○ Dependent on soil depth

	Hydrology	Solute Mass	Concentration
Frequency of Output:	Yearly	Yearly	Yearly
Output for Every ... th Layer:	1	1	1

Figure 33: PELMO 5.0 Soil scenario form: soil

As a consequence also soil moistures above field capacities could be simulated when using that option. Dependent on the selection the input form for the soil profile information is adapted accordingly (Figure 34).

To specify the detailed soil profile data the button “Soil Horizon Parameters” has to be pressed (see the red arrow in Figure 33).



Horizon Number	Thickness [cm]	Bulk Density [kg/L]	Dispersion length [cm]	Initial Soil Water [m³/m³]	Field Capacity [m³/m³]	Wilting Point [m³/m³]	Organic Carbon [%]	pH-Value	Biodeg. factor [-]
Horizon 1	30	1.29	5	0.304	0.304	0.086	4.06	6.2	1
Horizon 2	30	1.52	5	0.158	0.158	0.023	0.84	5.6	0.5
Horizon 3	35	1.64	5	0.151	0.151	0.021	0.36	5.4	0.3
Horizon 4	5	1.63	5	0.162	0.162	0.024	0.29	5.4	0.3
Horizon 5	20	1.63	5	0.162	0.162	0.024	0.29	5.4	0
Horizon 6	30	1.66	5	0.121	0.121	0.017	0.21	5.3	0

Figure 34: PELMO 5.0 Soil profile form

Dependent on previous settings the input form for the soil profile data (see Figure 34) may look differently.

Generally, there is at least one row for each horizon for thickness (cm), bulk density (kg/L), initial soil water content (m³/m³), organic carbon content (%), the pH-value and the biodegradation factor.

Dependent on the selection on the scenario input form they are additional columns asking for the dispersion coefficient (cm²/d) or the dispersion length (cm) and either sand and clay content (%) or field capacity and wilting point (m³/m³).

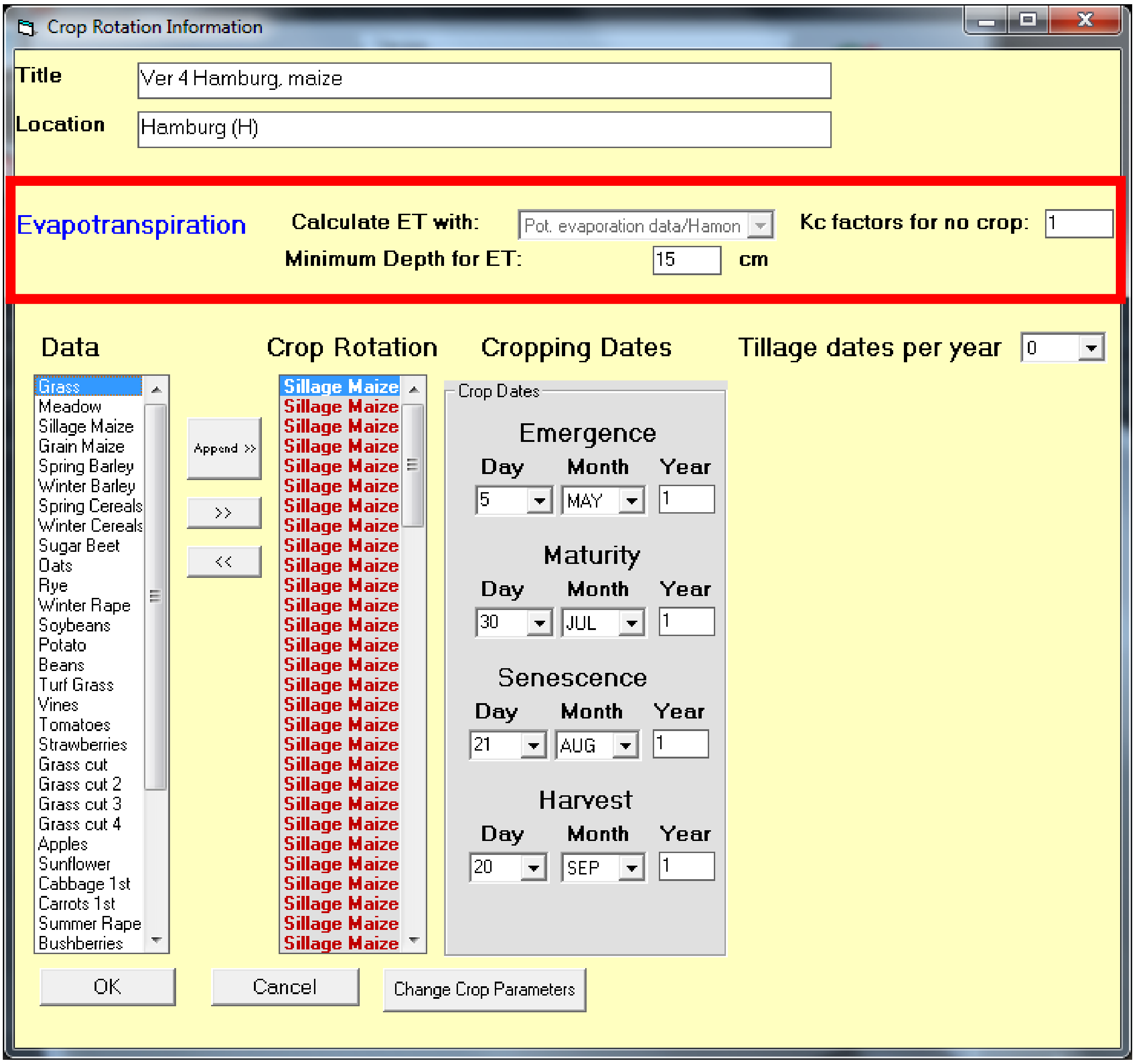
3.4.3 Defining the tabular output

In the bottom of the scenario input form (see Figure 33) the spatial and temporal resolution in the output tables can be defined. For the time resolution either “yearly”, “monthly” or “daily” can be set. For the spatial resolution the output can very between 1 (= output for every compartment) up to n (n=number of compartments, only for a single layer).

3.5 *Creating or modifying crop and crop rotation parameters*

When doing FOCUS groundwater or EFSA soil simulations the user should not change the crop and crop rotation information.

Nevertheless soil input files can be created either by double clicking at the respective crop rotation input file at the FOCUS or user specific part of the shell.



Title: Ver 4 Hamburg, maize

Location: Hamburg (H)

Calculate ET with: Pot. evaporation data/Hamon

Kc factors for no crop: 1

Minimum Depth for ET: 15 cm

Tillage dates per year: 0

Sillage Maize

	Day	Month	Year
Emergence	5	MAY	1
Maturity	30	JUL	1
Senescence	21	AUG	1
Harvest	20	SEP	1

Figure 35: PELMO 5.0 Crop rotation form

3.5.1 Evapotranspiration

The crop rotation form allows to set the necessary information to calculate evapotranspiration, run-off, preferential flow, soil erosion and crop related processes.

In previous version there were four options available to calculate actual evapotranspiration (see the red rectangle in Figure 35)

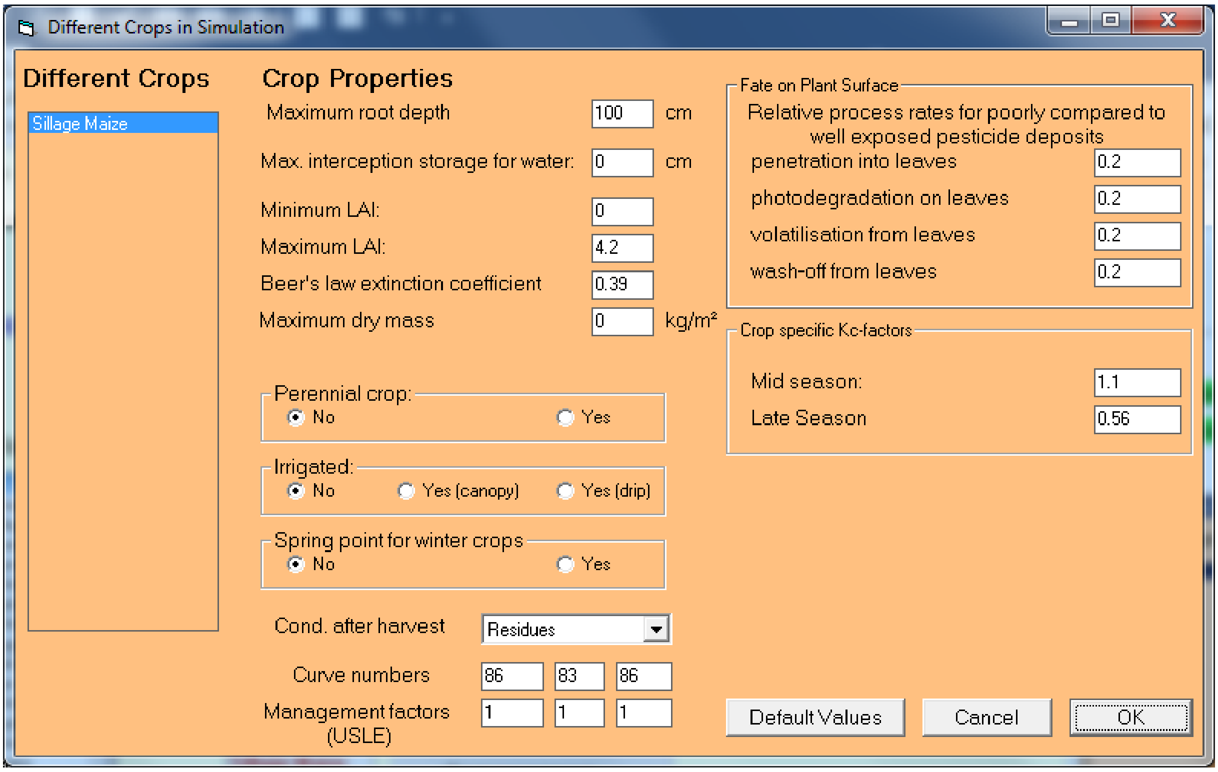
- Potential evapotranspiration data
- Hamon equation
- Potential evapotranspiration, if value missing use Hamon equation
- Haude equation

In the new version only the third options is still available. Basically that means that the Haude equation is not used anymore, because of the poor quality of the methodology. The preferred option is having available potential evapotranspiration data. If data on potential evapotranspiration is not available the Haude equation (based on temperature and light day hours) will be considered.

Further input parameters necessary to calculate actual evapotranspiration are the crop stage dependent kc-factors and the minimum depth to which is soil evaporation is extracted from if no crop is present.

3.5.2 Crop rotation

To add a crop to the rotation it has to be selected from the list on the left hand side of the form. For all crops in the list have predefined dates for emergence, maturation, senescence and harvest. However, dependent on the selected rotation the predefined values have to be corrected manually. Tillage dates can only be entered if the crop has been previously marked (“Tillage before emergence”). To change crop parameters the respective button on the rotation form has to be clicked. Tillage can be considered only for the whole simulation not for single crops only. Consequently, also a single tillage depth can be entered only for the whole simulation independent on the actual crop.



Sillage Maize

Maximum root depth: 100 cm
Max. interception storage for water: 0 cm
Minimum LAI: 0
Maximum LAI: 4.2
Beer's law extinction coefficient: 0.39
Maximum dry mass: 0 kg/m²

Perennial crop: ● No ○ Yes
Irrigated: ● No ○ Yes (canopy) ○ Yes (drip)
Spring point for winter crops: ● No ○ Yes

Cond. after harvest: Residues
Curve numbers: 86 83 86
Management factors (USLE): 1 1 1

Fate on Plant Surface
Relative process rates for poorly compared to well exposed pesticide deposits
penetration into leaves: 0.2
photodegradation on leaves: 0.2
volatilisation from leaves: 0.2
wash-off from leaves: 0.2

Crop specific Kc-factors
Mid season: 1.1
Late Season: 0.56

Figure 36: PELMO 5.0 Crop data form

3.5.3 *Crops*

Parameters for all crops selected on the crop rotation form can be individually changed. The crop parameters summarised in the top of the form represent the maximum values which together with the emergence and maturation dates are used to calculate the effect of crop growth.

- If a crop is marked as “perennial” the maximum rooting depth is considered directly after crop emergence.
- If a crop is marked as irrigated automatic irrigation will be calculated between emergence and senescence date.
- If a crop is having a spring point (winter crops) the development of the crop will not start after emergence but after reaching the spring point in the following year.

If the spring point box is checked the user should additionally enter its respective day and month.

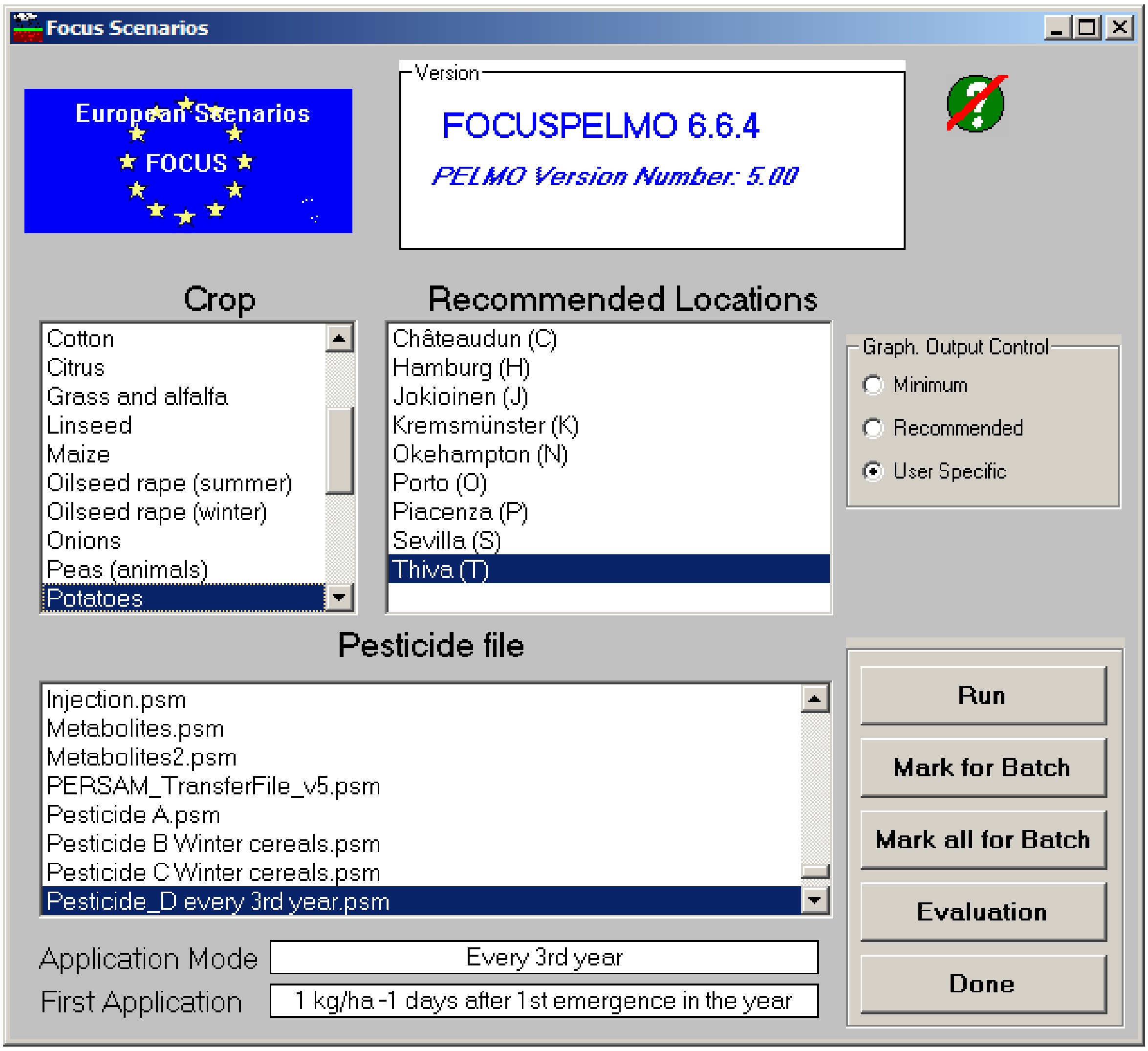
If run-off should be considered the RC-Numbers should be also given here.

In order to improve the quality of pesticide fate on plant surfaces the user can define relative process rates for poorly exposed pesticide deposits for four different processes (penetration into leaves, photo-degadation on leaves, volatilisation from leaves, wash-off from leaves). The distribution of the pesticide between well and poorly exposed deposits depends on the application input (see chapter 3.3).

3.6 Running FOCUS simulations

3.6.1 Introduction

Based on the shell WPELMO.EXE it is easy to perform PELMO-simulations. There is a special form (see Figure 37) which can be used to combine the different types of input data for simulations. There is no need to consider the standard warming up period of 6 six for FOCUS groundwater manually. The shell takes care that this period is always included and that all 80th percentiles are related to the correct period of 20, 50 or 60 years without the initial warming up period.. Also the decided to It is loaded after a click at the blue European flag on the main form with “FOCUS” on it (see Figure 10).



FOCUSPELMO 6.6.4

PELMO Version Number: 5.00

Crop:
Cotton
Citrus
Grass and alfalfa
Linseed
Maize
Oilseed rape (summer)
Oilseed rape (winter)
Onions
Peas (animals)
Potatoes

Recommended Locations:
Châteaudun (C)
Hamburg (H)
Jokioinen (J)
Kremsmünster (K)
Okehampton (N)
Porto (O)
Piacenza (P)
Sevilla (S)
Thiva (T)

Graph. Output Control:
○ Minimum
○ Recommended
● User Specific

Pesticide file:
Injection.psm
Metabolites.psm
Metabolites2.psm
PERSAM_TransferFile_v5.psm
Pesticide A.psm
Pesticide B Winter cereals.psm
Pesticide C Winter cereals.psm
Pesticide_D every 3rd year.psm

Application Mode: Every 3rd year

First Application: 1 kg/ha -1 days after 1st emergence in the year

Figure 37: PELMO 5.0 Combining FOCUS scenarios for a simulation

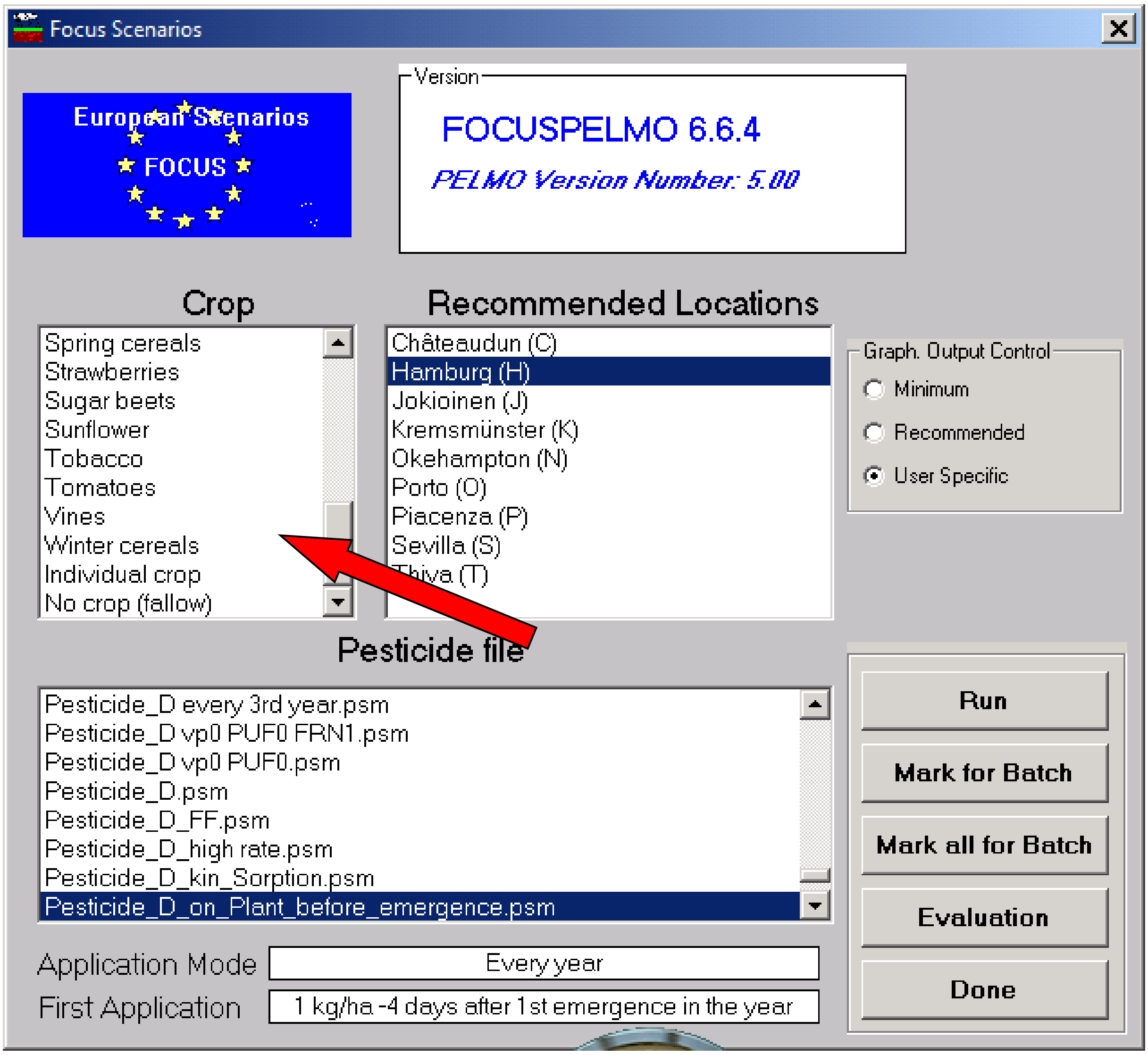
After having created the necessary pesticide input data file (see section 3.3) the user only has to select a suitable crop and at least one of the recommended locations as follows:

1. select the pesticide input file,
2. select the crop to be considered,
3. select the location to be simulated,
4. click at the “Run” button to start the simulation.

Instead of the “Run” button also “Mark for batch” can be used. Then, the combination is stored and further simulations can be prepared before running the simulations. The “Run” button changes to “Start batch” and should be used to start the batch job.
Finally, the user can also click at “Mark all for batch”. Then, all locations recommended for a certain crop are automatically considered for PELMO simulations. Again, to start the batch job the button “Start batch” has to be used.

The PELMO simulation will automatically start after clicking at the RUN button. The RUN-button is disabled if no application pattern has been defined earlier in the pesticide file for the specific location selected (a warning by the shell pops up in such a situation). When no regular application pattern was defined in the selected pesticide file (regular = the same application dates, rates, and depths in all individual simulation years) the RUN-button will also remain disabled.
As it is not possible to run two PELMO simulations at the same time the RUN-button will be disabled as long as the current simulation is running.
If the simulation fails the RUN-button remains disabled though there is no PELMO job active the use should shortly exit the shell. When returning, the RUN-button should be enabled again.

The FOCUS crop data files are generally protected and cannot be changed by users. However, for special situations (e.g. higher tier simulations with crop rotation considered) it may be useful to do a FOCUS simulation with modified crop parameters. To account for that the user can define an individual crop which can be found at the last item in the crop list (Figure 38). In contrast to standard FOCUS crops the definition of relative application dates is not possible for individual crops.



Version: FOCUSPELMO 6.6.4

PELMO Version Number: 5.00

Recommended Locations: Hamburg (H)

Graph. Output Control: User Specific

Pesticide file: Pesticide_D_on_Plant_before_emergence.psm

Application Mode: Every year

First Application: 1 kg/ha -4 days after 1st emergence in the year

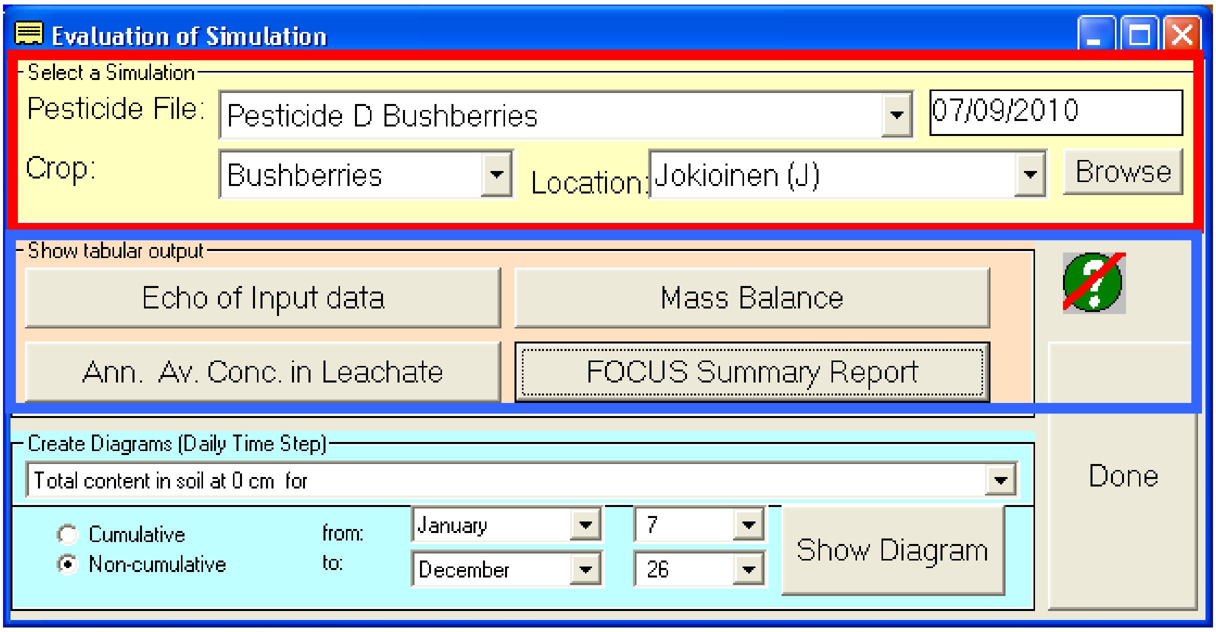
Figure 38: PELMO 5.0 Defining individual crops for FOCUS simulations

3.6.2 Archiving simulations

All FOCUS simulations are automatically copied into a special folder which is defined by the name of the pesticide file used and the crop-location-combination. Therefore, special archiving of simulations is not necessary. All simulations performed in the system can be analysed using the form “Evaluation of Simulations”. If the same pesticide file and the same crop-scenario combination are used again users will be warned that an existing simulation may be overwritten.

3.6.3 Post Processing of FOCUS-Simulations

After a FOCUS simulation successfully finished the results can be analysed by a special module which generates all important output for pesticides and metabolites (see Figure 39). It is loaded when using the button “Evaluation” at the FOCUS scenario form (Figure 37).
Usually the most recent PELMO simulation is loaded and appears at first at the form. However, by using the list boxes in the frame “Select a simulation” (see the red rectangle in Figure 37) the user can move to other simulations. The simulations are generally sorted hierarchically with the pesticide input file at the top level, followed by the crop and the location as the third level. Alternatively, simulation results can also be selected by using the “browse” button.



Pesticide File: Pesticide D Bushberries
07/09/2010
Crop: Bushberries
Location: Jokioinen (J)

Total content in soil at 0 cm for

○ Cumulative
● Non-cumulative

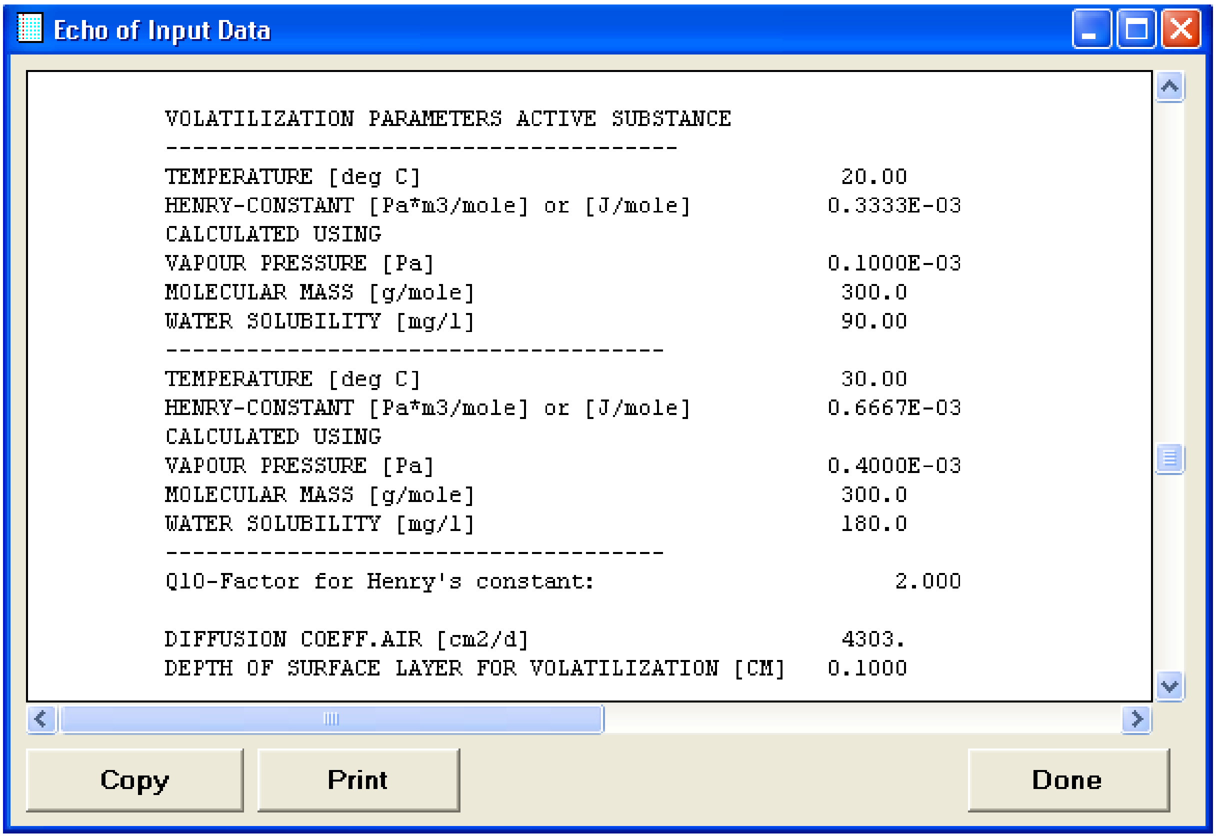
from: January 7
to: December 26

Figure 39: PELMO 5.0 Analysing FOCUS simulations using WPELMO.EXE

Four different types of tabular output is available when using the respective buttons (see the blue rectangle in Figure 39).

3.6.3.1 <u>Echo of Input Data</u>

The button “Echo of Input data” (see the blue rectangle in Figure 39) will load a form showing an echo of all input data considered for the simulation (see Figure 40). This information is also saved in an ascii-file called “echo.plm”. The form can be used to scroll through the file, to print this information or copy it into the clipboard.

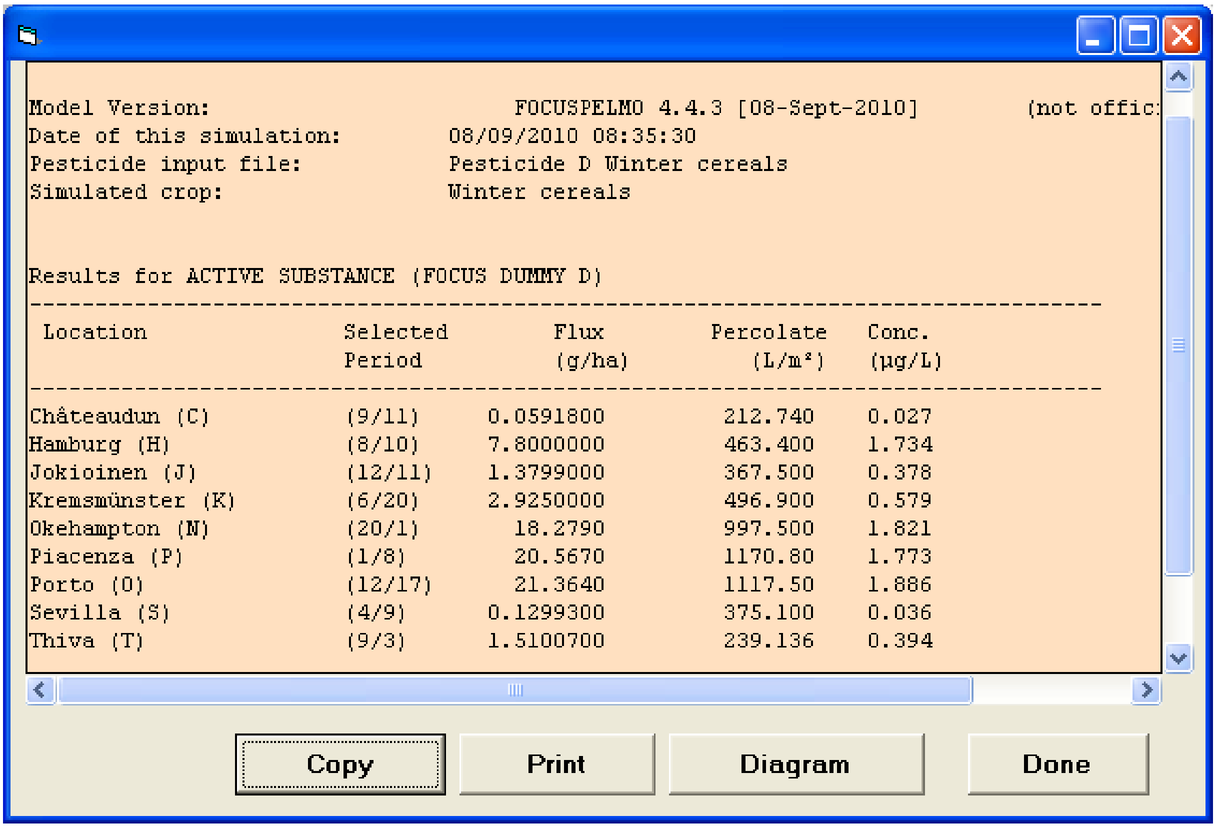


```
VOLATILIZATION PARAMETERS ACTIVE SUBSTANCE
--------------------------------------
TEMPERATURE [deg C]                          20.00
HENRY-CONSTANT [Pa*m3/mole] or [J/mole]     0.3333E-03
CALCULATED USING
VAPOUR PRESSURE [Pa]                        0.1000E-03
MOLECULAR MASS [g/mole]                      300.0
WATER SOLUBILITY [mg/l]                      90.00
-------------------------------------
TEMPERATURE [deg C]                          30.00
HENRY-CONSTANT [Pa*m3/mole] or [J/mole]     0.6667E-03
CALCULATED USING
VAPOUR PRESSURE [Pa]                        0.4000E-03
MOLECULAR MASS [g/mole]                      300.0
WATER SOLUBILITY [mg/l]                      180.0
-------------------------------------
Q10-Factor for Henry's constant:                 2.000

DIFFUSION COEFF.AIR [cm2/d]                  4303.
DEPTH OF SURFACE LAYER FOR VOLATILIZATION [CM]   0.1000
```

Figure 40: PELMO 5.0 Echo of all input data used for the simulation

3.6.3.2 FOCUS GW Summary Report

FOCUS summary reports present tabular results of the 80th percentile of the percolate concentration at 1 m soil depth according to the FOCUS recommendation. However, in contrast to the other evaluation tools the summary report does not only summarise results of the selected simulation but also respective results of the some crop at other locations. When using this button the form is loaded shown in Figure 41 is loaded. The form can be used to scroll through the file, to print this information or copy it into the clipboard.



```
Model Version:                     FOCUSPELMO 4.4.3 [08-Sept-2010]       (not offic:
Date of this simulation:        08/09/2010 08:35:30
Pesticide input file:           Pesticide D Winter cereals
Simulated crop:                 Winter cereals


Results for ACTIVE SUBSTANCE (FOCUS DUMMY D)
---------------------------------------------------------------------------------
 Location                Selected        Flux         Percolate   Conc.
                         Period          (g/ha)         (L/m²)    (µg/L)
---------------------------------------------------------------------------------
Châteaudun (C)           (9/11)     0.0591800         212.740    0.027
Hamburg (H)              (8/10)     7.8000000         463.400    1.734
Jokioinen (J)            (12/11)    1.3799000         367.500    0.378
Kremsmünster (K)         (6/20)     2.9250000         496.900    0.579
Okehampton (N)           (20/1)       18.2790         997.500    1.821
Piacenza (P)             (1/8)        20.5670         1170.80    1.773
Porto (O)                (12/17)      21.3640         1117.50    1.886
Sevilla (S)              (4/9)      0.1299300         375.100    0.036
Thiva (T)                (9/3)      1.5100700         239.136    0.394
```

Figure 41: PELMO 5.0 FOCUS GW Summary report

The concentrations can be also visualised in a diagram. It is loaded when clicking at the button “Diagram” in Figure 41. The diagram gives an overview about the series of periodical concentrations. It shows the 80th percentile of the percolate concentration at 1 m for all simulated locations and for all considered substances (parent compound and transformation products. In the diagram concentrations below 0.1 µg/L are represented by green bars, concentrations above 0.1 µg/L by red bars. When the diagram is first loaded it will always show the results for the active compound (see Figure 42). After a click at the graph the concentration for transformation products will be displayed (Figure 43).

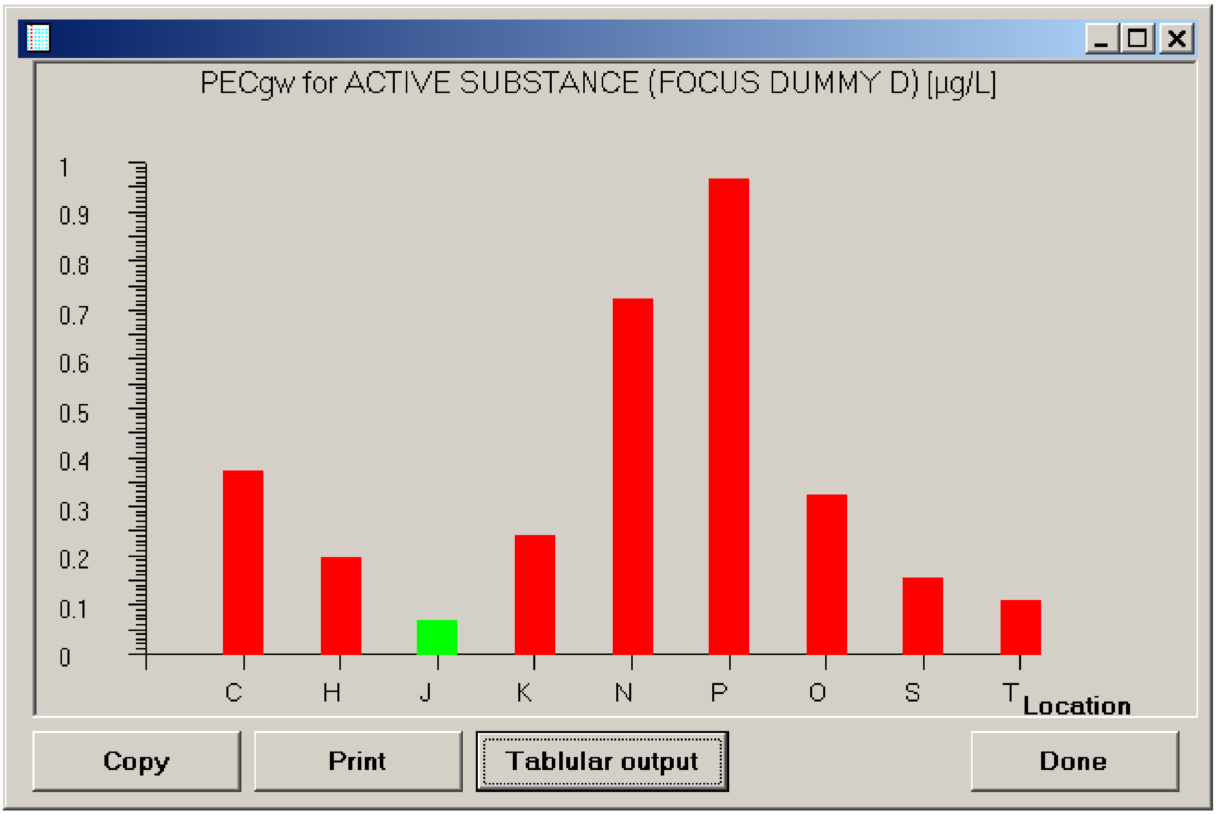


Figure 42: PELMO 5.0 Visualisation of the FOCUS Summary report for the parent compound

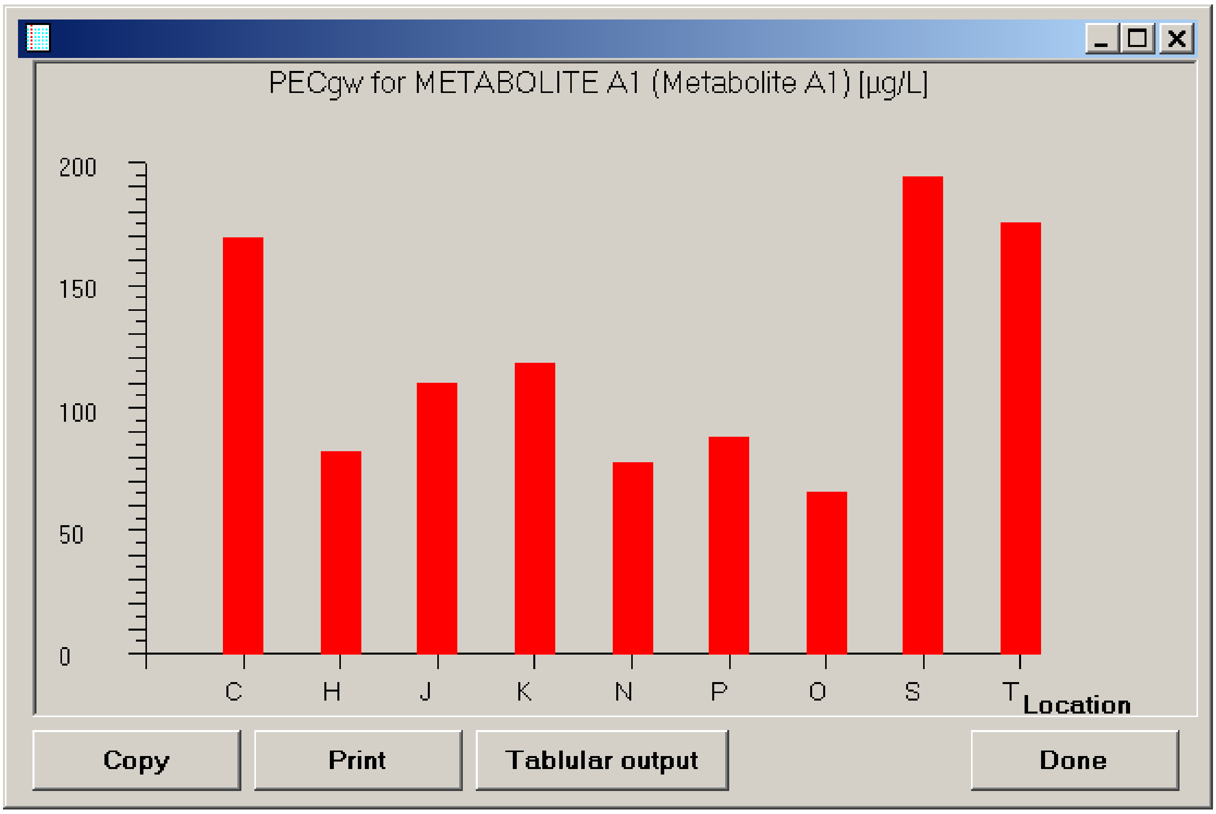
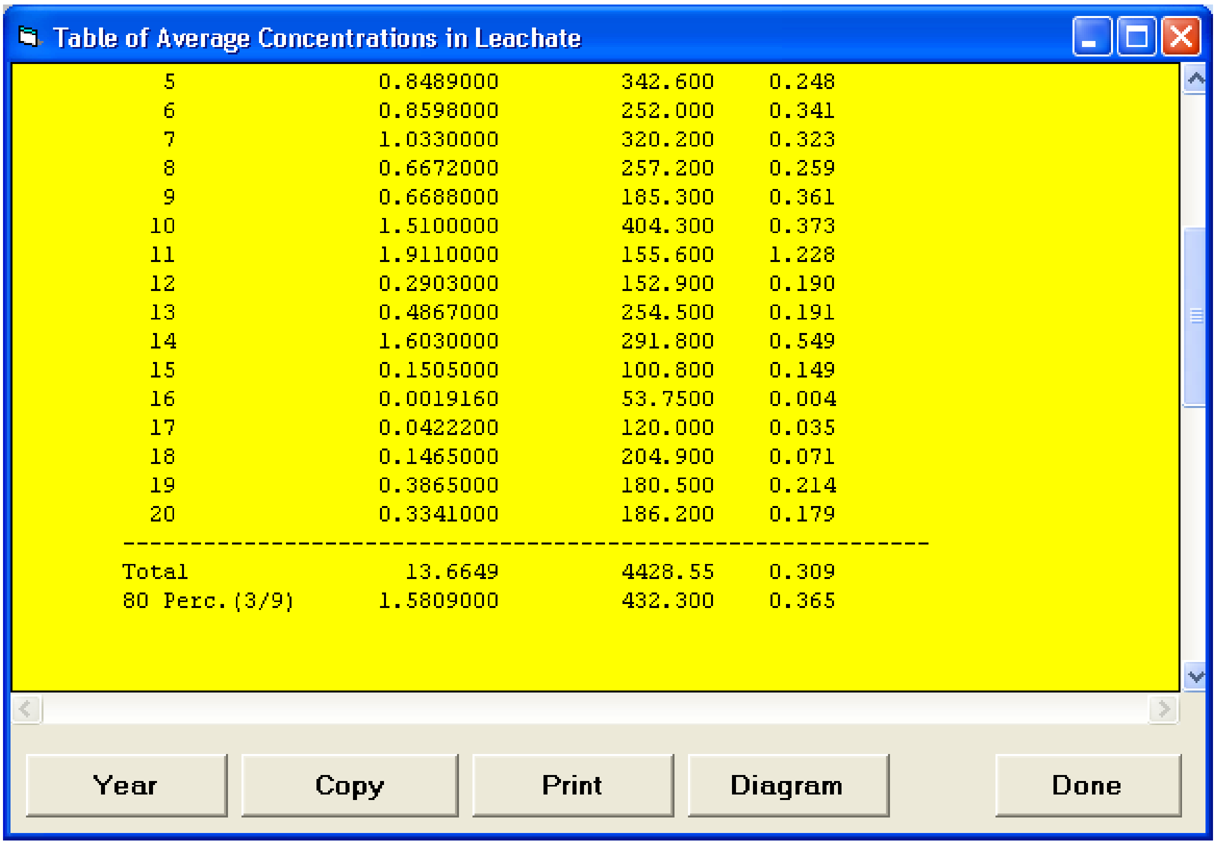


Figure 43: PELMO 5.0 Visualisation of the FOCUS Summary report for a metabolite

3.6.3.3 Annual average concentration in the leachate

The button “Annual av. concentration in the leachate” (blue rectangle in Figure 39) will load a form showing the percolate concentration of the active compound and all transformation products in annual and periodical resolution (see Figure 44). “Periodically” means annually, biennially, or triennially, dependent on the application frequency in the pesticide input file. Concentrations are given at a depth of 100 m and at the bottom of the soil core. Additionally the 80th percentile of the concentration is outputted as recommended by FOCUS. The numbers in brackets refer to the years for which the concentrations were simulated. All this information is also saved in ASCII-Files called “period.plm” and “year.plm”.

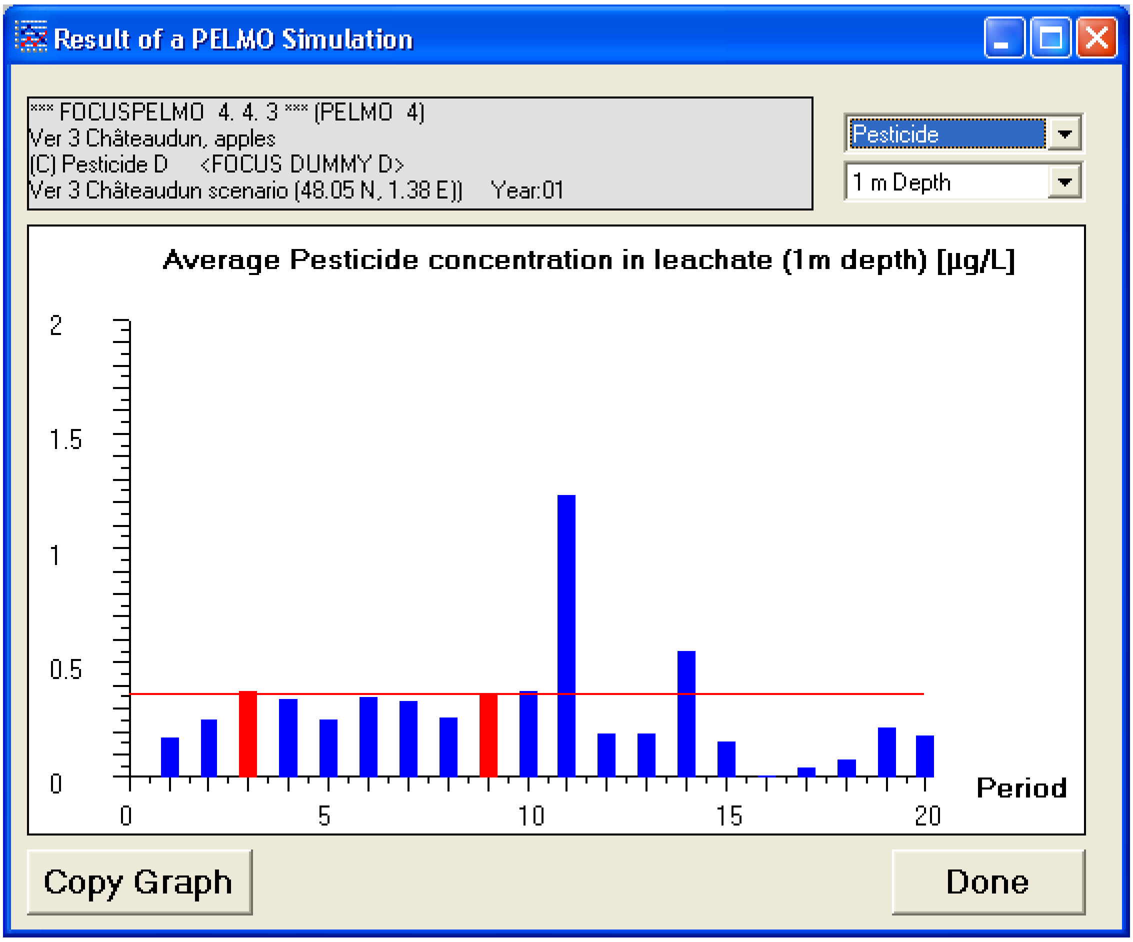
The form can be used to scroll through the file, to print this information or to copy it into the clipboard.



```
       5              0.8489000       342.600    0.248
       6              0.8598000       252.000    0.341
       7              1.0330000       320.200    0.323
       8              0.6672000       257.200    0.259
       9              0.6688000       185.300    0.361
      10              1.5100000       404.300    0.373
      11              1.9110000       155.600    1.228
      12              0.2903000       152.900    0.190
      13              0.4867000       254.500    0.191
      14              1.6030000       291.800    0.549
      15              0.1505000       100.800    0.149
      16              0.0019160       53.7500    0.004
      17              0.0422200       120.000    0.035
      18              0.1465000       204.900    0.071
      19              0.3865000       180.500    0.214
      20              0.3341000       186.200    0.179
    ------------------------------------------------------------
    Total               13.6649       4428.55    0.309
    80 Perc.(3/9)     1.5809000       432.300    0.365
```

Figure 44: PELMO 5.0 Tabular output of annual concentrations in the leachate

The annual or periodical information can be also visualised in a diagram. It will be loaded if the users clicks at the button “Diagram” in Figure 44. The diagram gives an overview about the series of periodical concentrations (see Figure 45). It can show either concentrations for the active substance or transformation products and at 1 m or at the soil bottom. The desired output can be selected via the two list boxes on the form. In the diagram the periods that were used to calculate the 80th percentile are marked together with a red line which represents the 80th percentile of the periodical concentration.

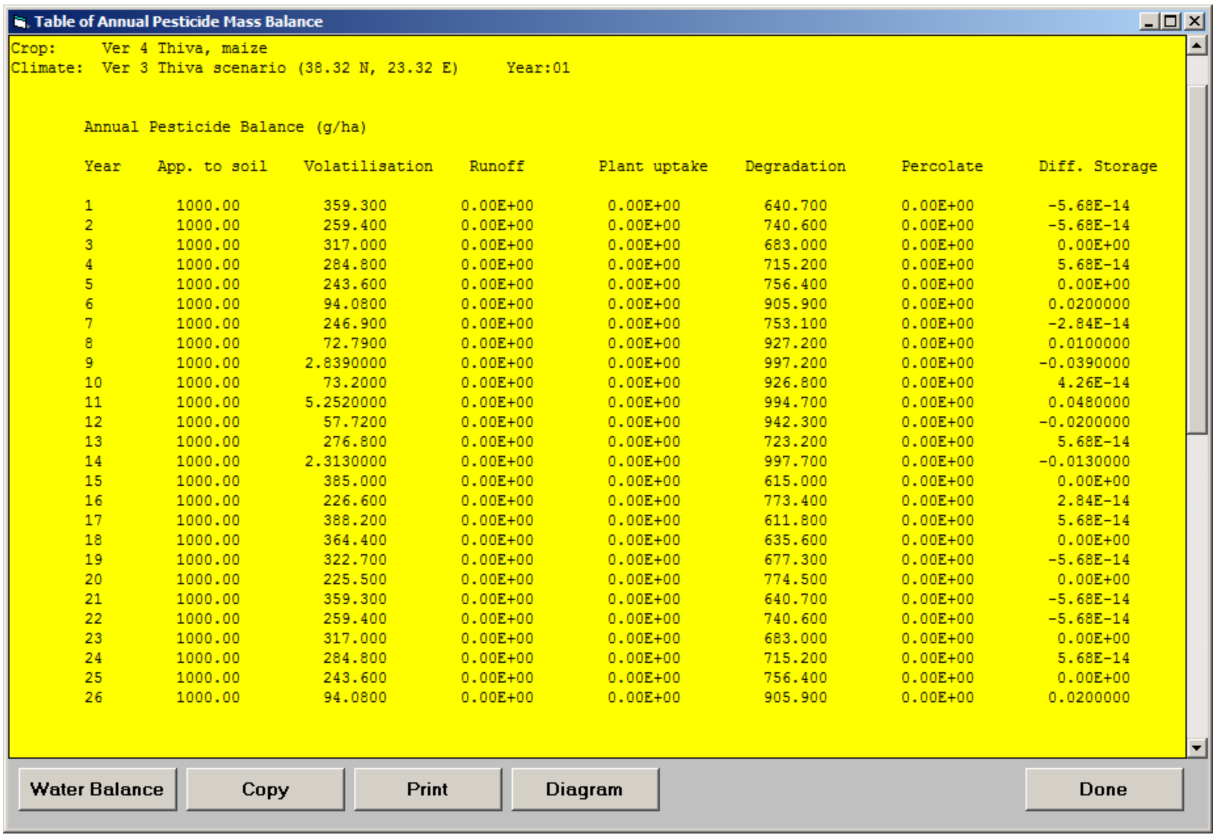


*** FOCUSPELMO 4. 4. 3 *** (PELMO 4)
Ver 3 Châteaudun, apples
(C) Pesticide D <FOCUS DUMMY D>
Ver 3 Châteaudun scenario (48.05 N, 1.38 E)) Year:01

Figure 45: PELMO 5.0 Graphical output of periodical concentrations in the leachate

3.6.3.4 Mass balance

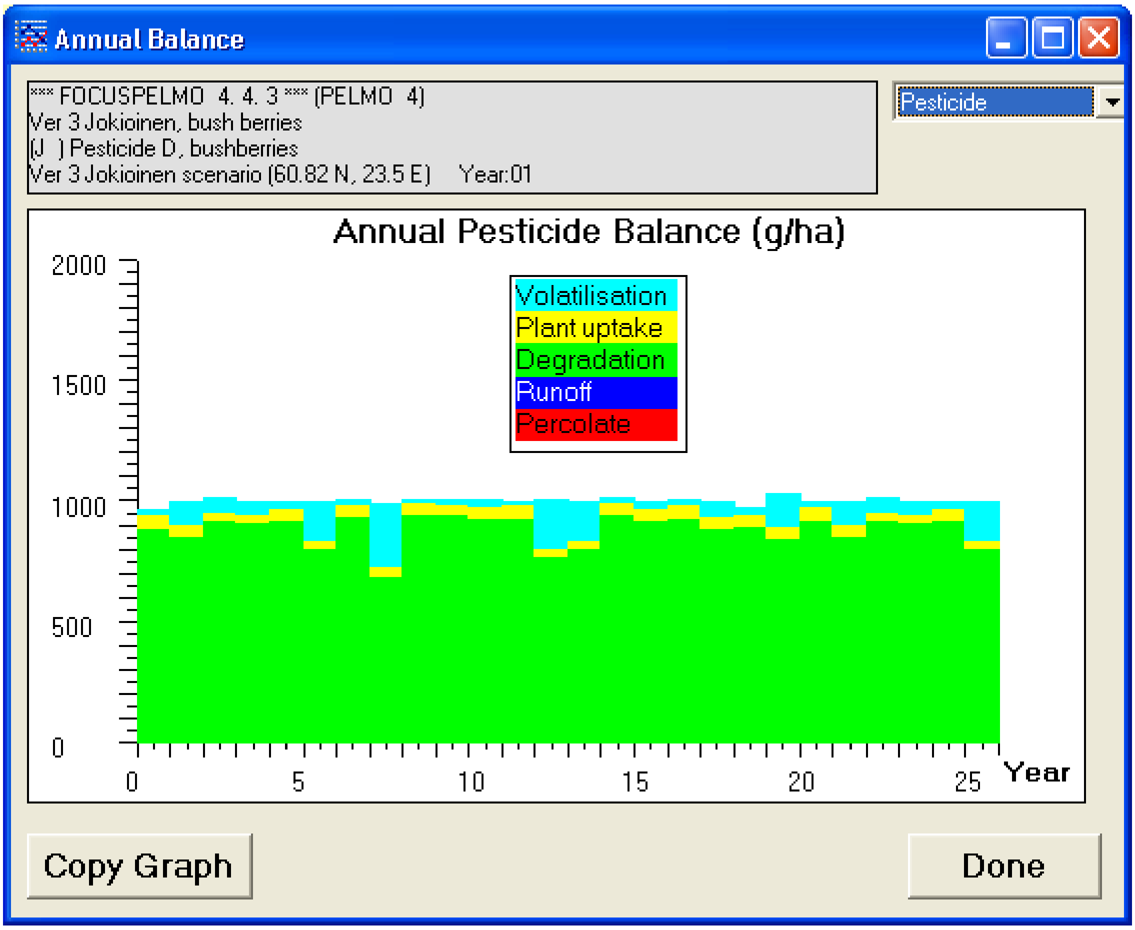
The button “Mass balance” (see the blue rectangle in Figure 39) will load a form showing the annual mass balance for water, the active compound and all transformation products. The table switches from hydrology to substances when using the left button. This information is also saved in ASCII-Files called “MBalance.plm” (hydrology) and “PBalance.plm” (substances). The form can be used to scroll through the file, to print this information, or to copy it into the clipboard.



```
Crop:     Ver 4 Thiva, maize
Climate:  Ver 3 Thiva scenario (38.32 N, 23.32 E)     Year:01


        Annual Pesticide Balance (g/ha)

        Year  App. to soil  Volatilisation        Runoff   Plant uptake    Degradation      Percolate   Diff. Storage

        1          1000.00         359.300      0.00E+00       0.00E+00        640.700       0.00E+00       -5.68E-14
        2          1000.00         259.400      0.00E+00       0.00E+00        740.600       0.00E+00       -5.68E-14
        3          1000.00         317.000      0.00E+00       0.00E+00        683.000       0.00E+00        0.00E+00
        4          1000.00         284.800      0.00E+00       0.00E+00        715.200       0.00E+00        5.68E-14
        5          1000.00         243.600      0.00E+00       0.00E+00        756.400       0.00E+00        0.00E+00
        6          1000.00         94.0800      0.00E+00       0.00E+00        905.900       0.00E+00       0.0200000
        7          1000.00         246.900      0.00E+00       0.00E+00        753.100       0.00E+00       -2.84E-14
        8          1000.00         72.7900      0.00E+00       0.00E+00        927.200       0.00E+00       0.0100000
        9          1000.00       2.8390000      0.00E+00       0.00E+00        997.200       0.00E+00      -0.0390000
        10         1000.00         73.2000      0.00E+00       0.00E+00        926.800       0.00E+00        4.26E-14
        11         1000.00       5.2520000      0.00E+00       0.00E+00        994.700       0.00E+00       0.0480000
        12         1000.00         57.7200      0.00E+00       0.00E+00        942.300       0.00E+00      -0.0200000
        13         1000.00         276.800      0.00E+00       0.00E+00        723.200       0.00E+00        5.68E-14
        14         1000.00       2.3130000      0.00E+00       0.00E+00        997.700       0.00E+00      -0.0130000
        15         1000.00         385.000      0.00E+00       0.00E+00        615.000       0.00E+00        0.00E+00
        16         1000.00         226.600      0.00E+00       0.00E+00        773.400       0.00E+00        2.84E-14
        17         1000.00         388.200      0.00E+00       0.00E+00        611.800       0.00E+00        5.68E-14
        18         1000.00         364.400      0.00E+00       0.00E+00        635.600       0.00E+00        0.00E+00
        19         1000.00         322.700      0.00E+00       0.00E+00        677.300       0.00E+00       -5.68E-14
        20         1000.00         225.500      0.00E+00       0.00E+00        774.500       0.00E+00        0.00E+00
        21         1000.00         359.300      0.00E+00       0.00E+00        640.700       0.00E+00       -5.68E-14
        22         1000.00         259.400      0.00E+00       0.00E+00        740.600       0.00E+00       -5.68E-14
        23         1000.00         317.000      0.00E+00       0.00E+00        683.000       0.00E+00        0.00E+00
        24         1000.00         284.800      0.00E+00       0.00E+00        715.200       0.00E+00        5.68E-14
        25         1000.00         243.600      0.00E+00       0.00E+00        756.400       0.00E+00        0.00E+00
        26         1000.00         94.0800      0.00E+00       0.00E+00        905.900       0.00E+00       0.0200000
```

Figure 46: PELMO 5.0 Tabular output of annual mass balance

The annual mass balances can be also visualised in additional diagrams. They are loaded when clicking at the button “Diagram” in Figure 46.



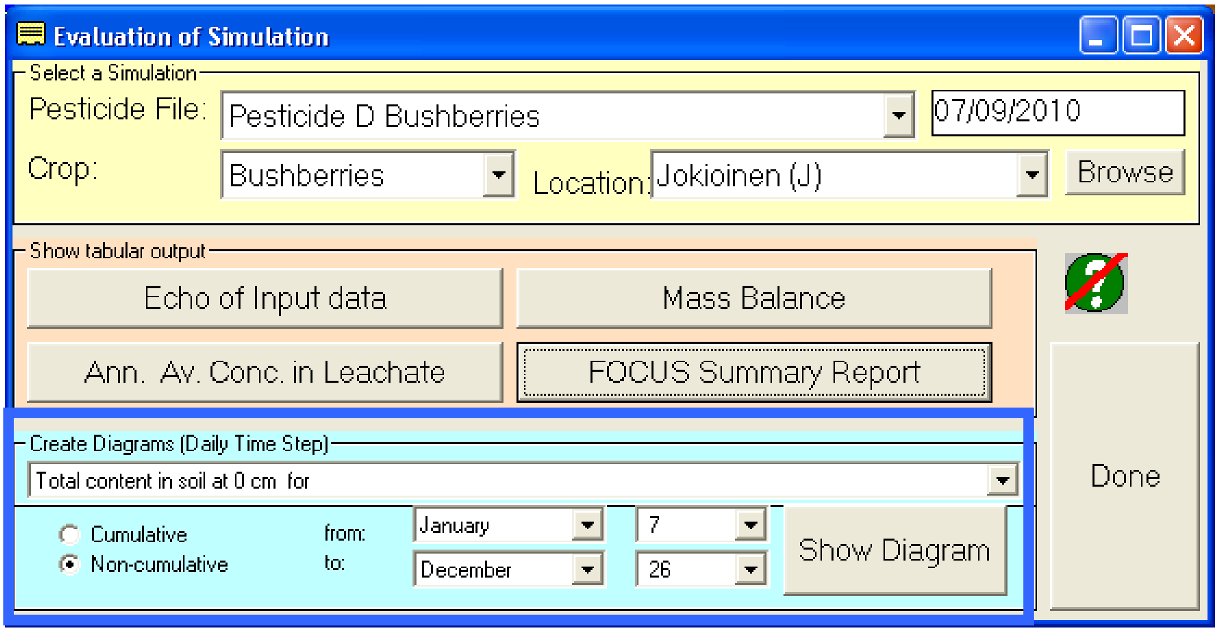
*** FOCUSPELMO 4. 4. 3 *** (PELMO 4)
Ver 3 Jokioinen, bush berries
(J) Pesticide D, bushberries
Ver 3 Jokioinen scenario (60.82 N, 23.5 E) Year:01

Figure 47: PELMO 5.0 Graphical representation of the annual mass balance

The diagram gives an overview annual mass balance (see Figure 47). It can show the annual masses for water, the active substance or transformation products. The desired output can be selected via the list box on the form.

3.6.3.5 Graphic representation of important parameters in daily resolution

Dependent on the selection made before running the simulation (see chapter 3.9) a number of diagrams can be produced in daily resolution (see the blue rectangle in Figure 48). A list of the previously selected parameters is provided in the list box. The series can be presented cumulatively or non-cumulatively. Also the period can be selected individually. The diagram is loaded when clicking at the button “show diagram” (Figure 49).



Pesticide File: Pesticide D Bushberries

07/09/2010

Crop: Bushberries

Location: Jokioinen (J)

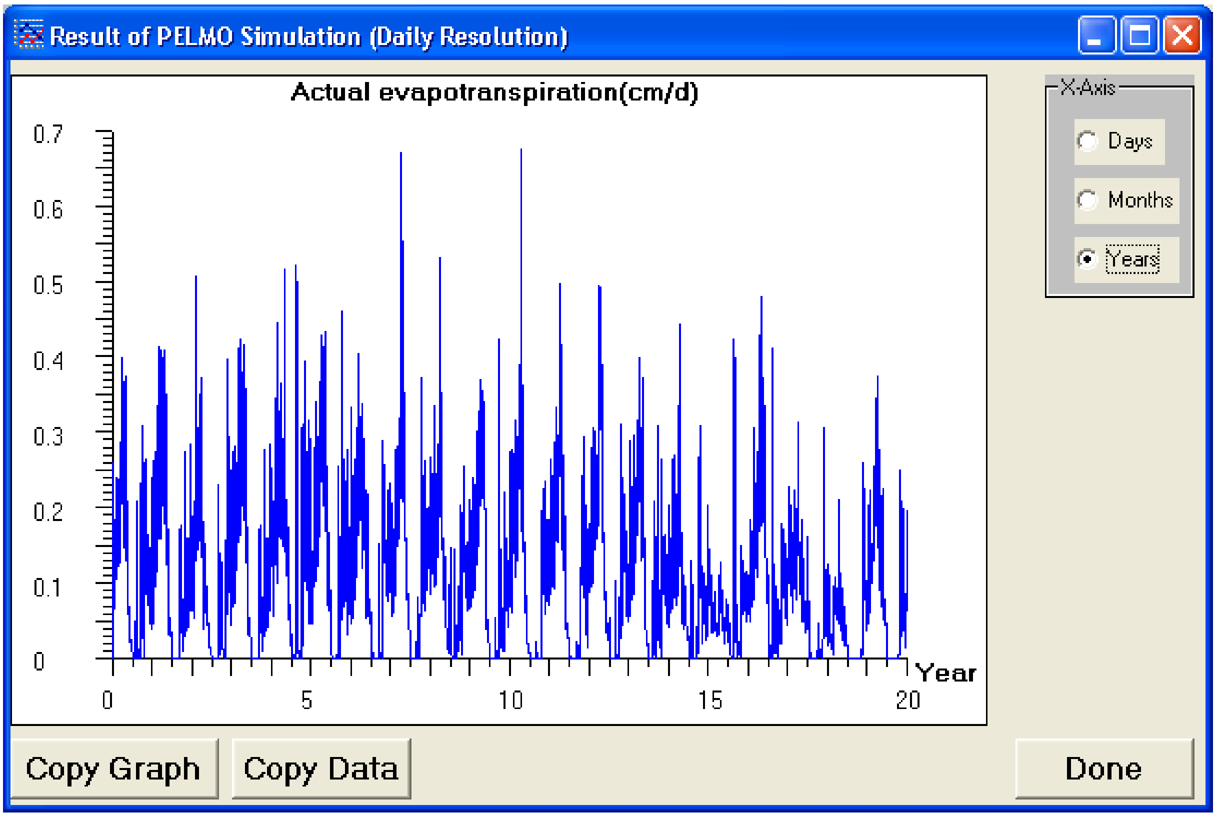
Total content in soil at 0 cm for

○ Cumulative
● Non-cumulative

from: January 7

to: December 26

Figure 48: PELMO 5.0 Analysing FOCUS simulations using WPELMO.EXE



○ Days
○ Months
● Years

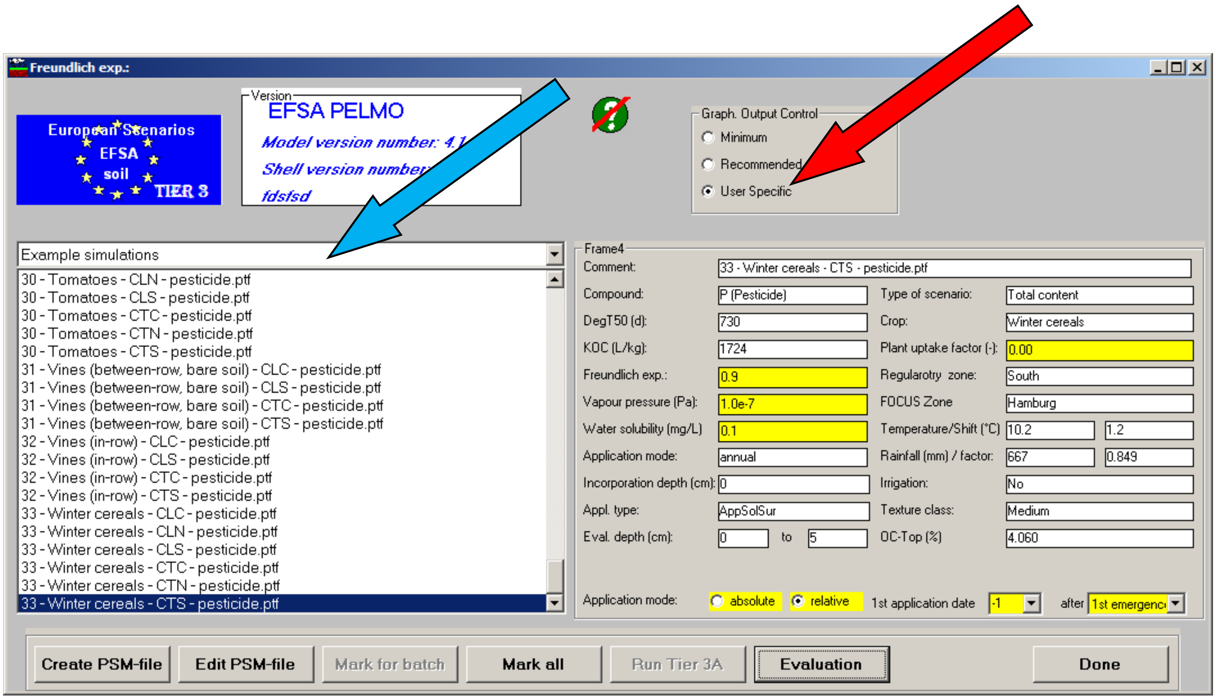
Figure 49: PELMO 5.0 Time series diagram of FOCUS results

The unit of the x-axis can be selected (days, months, years). Either the graph as bitmap or the tabular content can be copied into the clipboard.

3.7 Running EFSA Tier 3A simulations

3.7.1 Introduction

Tier 3A in PELMO offers the possibility of simulating exposure concentrations for crop- and substance-specific scenarios. Before running these type of simulations the user has to use the PERSAM tool (Decorte et al 2014) and create a PERSAM transfer file. These transfer files are representing a single situation with regard to substance properties, application pattern, crop and location. However, it is expected that more than one situation will be simulated with PELMO. Therefore, all situations of the same problem can be gathered as a project. The project folder should have the extension .prj and should be created in a subfolder of PELMO installation called “PERSAM_TRANSFER”.



Example simulations

30 - Tomatoes - CLN - pesticide.ptf
30 - Tomatoes - CLS - pesticide.ptf
30 - Tomatoes - CTC - pesticide.ptf
30 - Tomatoes - CTN - pesticide.ptf
30 - Tomatoes - CTS - pesticide.ptf
31 - Vines (between-row, bare soil) - CLC - pesticide.ptf
31 - Vines (between-row, bare soil) - CLS - pesticide.ptf
31 - Vines (between-row, bare soil) - CTC - pesticide.ptf
31 - Vines (between-row, bare soil) - CTS - pesticide.ptf
32 - Vines (in-row) - CLC - pesticide.ptf
32 - Vines (in-row) - CLS - pesticide.ptf
32 - Vines (in-row) - CTC - pesticide.ptf
32 - Vines (in-row) - CTS - pesticide.ptf
33 - Winter cereals - CLC - pesticide.ptf
33 - Winter cereals - CLN - pesticide.ptf
33 - Winter cereals - CLS - pesticide.ptf
33 - Winter cereals - CTC - pesticide.ptf
33 - Winter cereals - CTN - pesticide.ptf
33 - Winter cereals - CTS - pesticide.ptf

Comment: 33 - Winter cereals - CTS - pesticide.ptf

Compound:	P (Pesticide)	Type of scenario:	Total content
DegT50 (d):	730	Crop:	Winter cereals
KOC (L/kg):	1724	Plant uptake factor (-):	0.00
Freundlich exp.:	0.9	Regularotry zone:	South
Vapour pressure (Pa):	1.0e-7	FOCUS Zone	Hamburg
Water solubility (mg/L)	0.1	Temperature/Shift (°C)	10.2 / 1.2
Application mode:	annual	Rainfall (mm) / factor:	667 / 0.849
Incorporation depth (cm):	0	Irrigation:	No
Appl. type:	AppSolSur	Texture class:	Medium
Eval. depth (cm):	0 to 5	OC-Top (%)	4.060

Application mode: ○ absolute ● relative 1st application date -1 after 1st emergenc

Figure 50: PELMO 5.0 Preparing EFSA Tier 3A scenarios for a simulation

When the user calls the EFSA Tier 3A part of the shell all projects in the PERSAM_TRANSFER folder are listed and can be selected using the respective listbox (see the blue arrow in Figure 50). In the list below all transfer files are given. The shell automatically reads the content of the PERSAM file and presents the most important settings in the box in the right part of the shell. Most of the parameters needed for the simulations are already provided by PERSAM. That means that the user does not have to define any scenario specific information. It is all directly transferred. The shell is also able to create a pesticide input file for the simulations (PSM file).

However, there are some pesticide related parameters needed in PELMO which cannot be processed through PERSAM. For these parameters default values are suggested:

- Freundlich exponent (default: 0.9)
- Vapour pressure (default value: 0.0001 Pa)
- Water solubility (default value: 90 mg/L)
- First application date (default: relative, 1 day before emergence)
- Plant uptake factor (default: 0.5)

As shown in Figure 50 these parameters are marked with yellow background colour. These fields can be directly modified on this form by the user without loading the complete input form for PSM files (see Figure 11)

If the user accepts the suggested the button “Create PSM-file” will induce the creation of the respective PSM in the PELMO program directory and the simulation can be performed afterwards. Alternatively, the user can further changes some pesticide input parameters using the complete input form (button: edit PSM-file). When all input files of the project has been created a batch file can be created by clicking at “Mark all”. “Start batch” will induce the batch job. If only a single run should be performed the button “Run Tier 3A” can be used without marking files for batch processing.

The Tier 3 scenarios are based on a time series of 20 years of daily meteorological information, such as rainfall and temperature. As described previously FOCUS used a warming-up period of 6 years in the leaching simulations before starting the 20-year evaluation period. However, in EFSA (2015) it was decided to use a longer warming-up period to ensure that the plateau value of the exposure concentration is always closely approximated before the evaluation starts. Therefore, the length of the warming-up period was re-evaluated by EFSA. It was concluded that the warming-up period ranged between 6 and 54 years, depending on the K_{oc} and *DegT50* of the substance (Table 6). Please notice that the half-life depends on soil temperature, so the half-lives in Table 6 refer to the half-life at the average scenario temperature.

Table 6: Warming-up periods (years) needed to reach the plateau concentration as a function of DegT50 (days) and Koc (L/kg).

DegT50 (d)	Koc < 172 L/kg	172 L/kg ≤ Koc < 862 L/kg	Koc ≥ 862 L/kg
DegT50 < 100 d	6	6	6
100 ≤ DegT50 < 200 d	12	12	12
200 ≤ DegT50 < 500 d	12	24	30
500 ≤ DegT50 < 1000 d	18	30	30
DegT50 ≥ 1000 d	24	30	54

According to EFSA (2015) always the same time series of six years has to be used.

As shown in Table 6 the warming-up period consists of a multiple of six years. Each six-year period should consist of the same meteorological time series. As it is important that this six-year time series has an approximately "average" air temperature the actual weather years depend on the location of the scenario.

Following time series for the warming-up period were selected by EFSA (see EFSA 2015)

Total content, North:	1912–1917;
Total content, Central:	1907–1912;
Total content, South:	1907–1912;
Porewater, North:	1909–1914;
Porewater, Central:	1907–1912;
Porewater, South:	1921–1926.

The new version of PELMO automatically applies the appropriate warming-up period, based on the K_{oc} and *DegT50* of the parent and transformation products so the user does not need to input the length of the warming-up period. Furthermore, the shell adds an additional year to the simulations without any applications to calculate the fading out of the concentrations when no applications are performed.

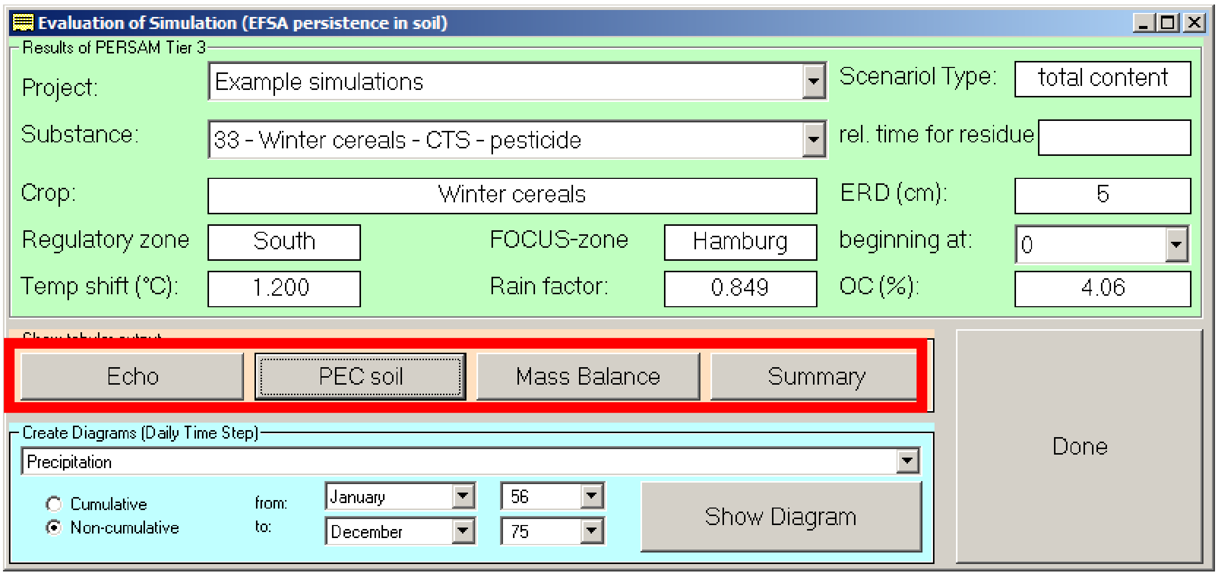
3.7.2 Archiving simulations

All EFSA Tier 3B simulations are automatically copied into a special folder which is defined by the name of the pesticide file used and the crop-location-combination. Therefore, special archiving of simulations is not necessary. All simulations performed in the system can be analysed using the form “Evaluation of Simulations”. If the same pesticide file and the same crop-scenario combination are used again users will be warned that an existing simulation may be overwritten.

3.7.3 Post Processing of EFSA Tier 3A-Simulations

After an EFSA soil Tier 3A simulation successfully finished the results can be analysed by a special module which generates all important output for the assessed compound (see Figure 51). It is loaded when using the button “Evaluation” at the EFSA Tier 3A scenario form (Figure 50).

The evaluation is always performed for a single run of a certain project. Consequently, the user has to specify the project and the respective situation.



Results of PERSAM Tier 3
Project: Example simulations
Scenariol Type: total content
Substance: 33 - Winter cereals - CTS - pesticide
rel. time for residue
Crop: Winter cereals
ERD (cm): 5
Regulatory zone South
FOCUS-zone Hamburg
beginning at: 0
Temp shift (°C): 1.200
Rain factor: 0.849
OC (%): 4.06

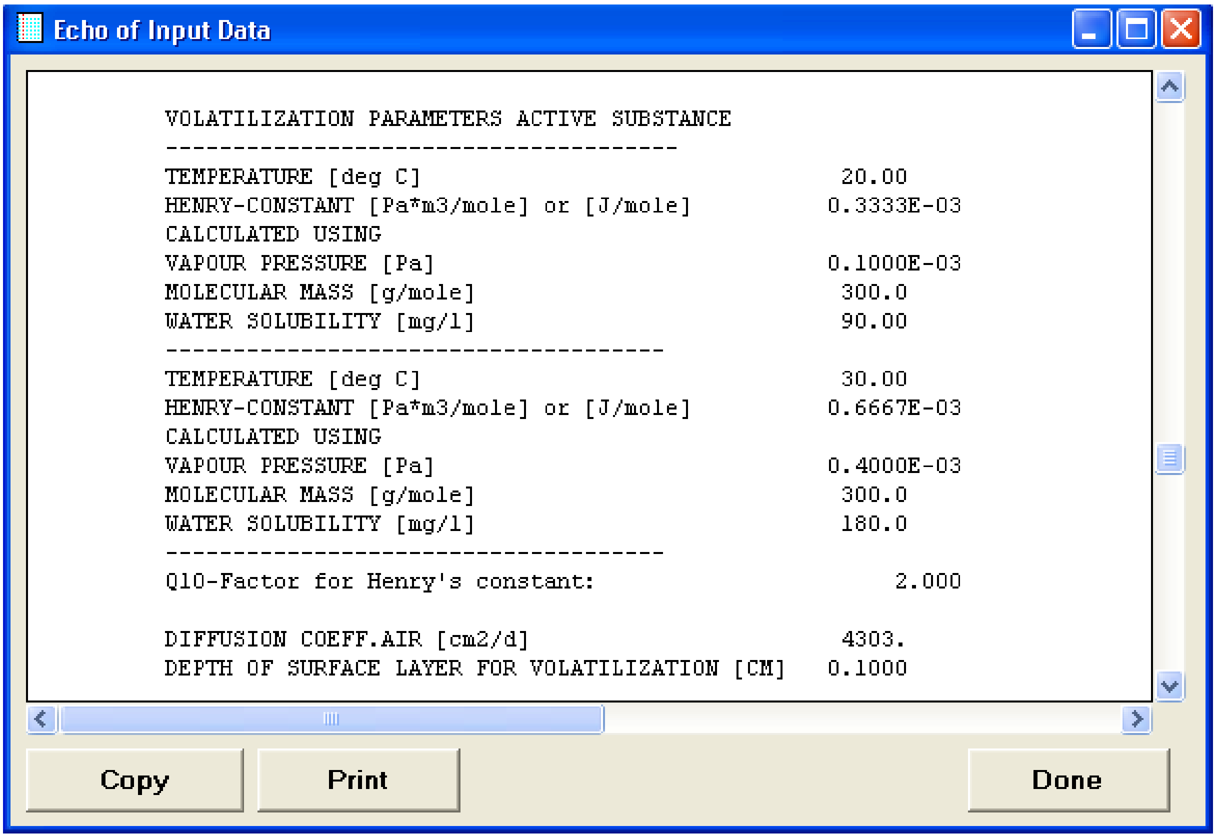
Create Diagrams (Daily Time Step)
Precipitation
○ Cumulative
● Non-cumulative
from: January 56
to: December 75

Figure 51: PELMO 5.0 Analysing EFSA Tier 3A simulations using WPELMO.EXE

Four different types of tabular output is available expressed by four buttons as shown in the red part of the form (see Figure 51).

3.7.3.1 <u>Echo of Input Data</u>

The button “Echo of Input data” in the red part of the evaluation form (see Figure 51) will present echo of all input data considered for the simulation (see Figure 52). This information is also saved in an ASCI-file called “echo.plm”. The form can be used to scroll through the file, to print this information or copy it into the clipboard.

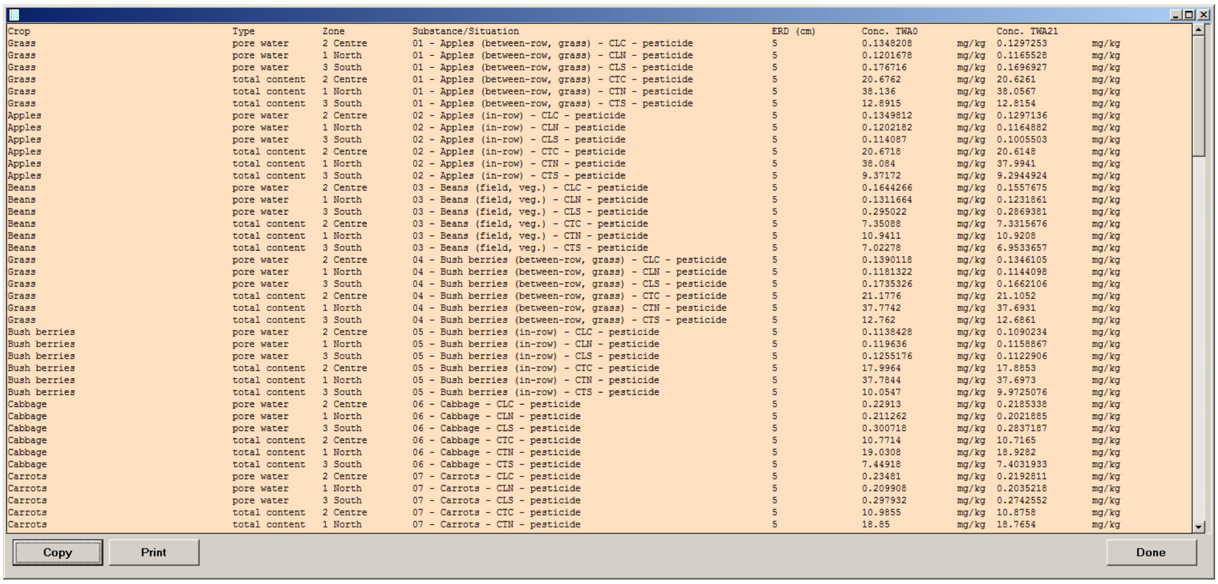


```
VOLATILIZATION PARAMETERS ACTIVE SUBSTANCE
--------------------------------------
TEMPERATURE [deg C]                             20.00
HENRY-CONSTANT [Pa*m3/mole] or [J/mole]        0.3333E-03
CALCULATED USING
VAPOUR PRESSURE [Pa]                           0.1000E-03
MOLECULAR MASS [g/mole]                         300.0
WATER SOLUBILITY [mg/l]                         90.00
-------------------------------------
TEMPERATURE [deg C]                             30.00
HENRY-CONSTANT [Pa*m3/mole] or [J/mole]        0.6667E-03
CALCULATED USING
VAPOUR PRESSURE [Pa]                           0.4000E-03
MOLECULAR MASS [g/mole]                         300.0
WATER SOLUBILITY [mg/l]                         180.0
-------------------------------------
Q10-Factor for Henry's constant:                    2.000

DIFFUSION COEFF.AIR [cm2/d]                     4303.
DEPTH OF SURFACE LAYER FOR VOLATILIZATION [CM]  0.1000
```

Figure 52: PELMO 5.0 Echo of all input data used for the simulation

3.7.3.2 Tier 3A Summary Report

The button “Summary” will present tabular results of the PEC soil concentrations for all situations of a project. When using this button the form is loaded shown in is loaded. Dependent on the number of individual simulations in the projects that it may take a coupble of minutes to provide the information The form can be used to scroll through the file, to print this information or copy it into the clipboard. The information is also automatically saved in a file called Summary_PEC.plm which can be found in the folder of the related project.



```
Crop                                Type          Zone           Substance/Situation                                      ERD (cm)       Conc. TWA0                Conc. TWA21
Grass                               pore water    2 Centre       01 - Apples (between-row, grass) - CLC - pesticide       5              0.1348208      mg/kg 0.1297253      mg/kg
Grass                               pore water    1 North        01 - Apples (between-row, grass) - CLN - pesticide       5              0.1201678      mg/kg 0.1165528      mg/kg
Grass                               pore water    3 South        01 - Apples (between-row, grass) - CLS - pesticide       5              0.176716       mg/kg 0.1696927      mg/kg
Grass                               total content 2 Centre       01 - Apples (between-row, grass) - CTC - pesticide       5              20.6762        mg/kg 20.6261        mg/kg
Grass                               total content 1 North        01 - Apples (between-row, grass) - CTN - pesticide       5              38.136         mg/kg 38.0567        mg/kg
Grass                               total content 3 South        01 - Apples (between-row, grass) - CTS - pesticide       5              12.8915        mg/kg 12.8154        mg/kg
Apples                              pore water    2 Centre       02 - Apples (in-row) - CLC - pesticide                   5              0.1349812      mg/kg 0.1297136      mg/kg
Apples                              pore water    1 North        02 - Apples (in-row) - CLN - pesticide                   5              0.1202182      mg/kg 0.1164882      mg/kg
Apples                              pore water    3 South        02 - Apples (in-row) - CLS - pesticide                   5              0.114087       mg/kg 0.1005503      mg/kg
Apples                              total content 2 Centre       02 - Apples (in-row) - CTC - pesticide                   5              20.6718        mg/kg 20.6148        mg/kg
Apples                              total content 1 North        02 - Apples (in-row) - CTN - pesticide                   5              38.084         mg/kg 37.9941        mg/kg
Apples                              total content 3 South        02 - Apples (in-row) - CTS - pesticide                   5              9.37172        mg/kg 9.2944924      mg/kg
Beans                               pore water    2 Centre       03 - Beans (field, veg.) - CLC - pesticide               5              0.1644266      mg/kg 0.1557675      mg/kg
Beans                               pore water    1 North        03 - Beans (field, veg.) - CLN - pesticide               5              0.1311664      mg/kg 0.1231861      mg/kg
Beans                               pore water    3 South        03 - Beans (field, veg.) - CLS - pesticide               5              0.295022       mg/kg 0.2869381      mg/kg
Beans                               total content 2 Centre       03 - Beans (field, veg.) - CTC - pesticide               5              7.35088        mg/kg 7.3315676      mg/kg
Beans                               total content 1 North        03 - Beans (field, veg.) - CTN - pesticide               5              10.9411        mg/kg 10.9208        mg/kg
Beans                               total content 3 South        03 - Beans (field, veg.) - CTS - pesticide               5              7.02278        mg/kg 6.9533657      mg/kg
Grass                               pore water    2 Centre       04 - Bush berries (between-row, grass) - CLC - pesticide 5              0.1390118      mg/kg 0.1346105      mg/kg
Grass                               pore water    1 North        04 - Bush berries (between-row, grass) - CLN - pesticide 5              0.1181322      mg/kg 0.1144098      mg/kg
Grass                               pore water    3 South        04 - Bush berries (between-row, grass) - CLS - pesticide 5              0.1735326      mg/kg 0.1662106      mg/kg
Grass                               total content 2 Centre       04 - Bush berries (between-row, grass) - CTC - pesticide 5              21.1776        mg/kg 21.1052        mg/kg
Grass                               total content 1 North        04 - Bush berries (between-row, grass) - CTN - pesticide 5              37.7742        mg/kg 37.6931        mg/kg
Grass                               total content 3 South        04 - Bush berries (between-row, grass) - CTS - pesticide 5              12.762         mg/kg 12.6861        mg/kg
Bush berries                        pore water    2 Centre       05 - Bush berries (in-row) - CLC - pesticide             5              0.1138428      mg/kg 0.1090234      mg/kg
Bush berries                        pore water    1 North        05 - Bush berries (in-row) - CLN - pesticide             5              0.119636       mg/kg 0.1158867      mg/kg
Bush berries                        pore water    3 South        05 - Bush berries (in-row) - CLS - pesticide             5              0.1255176      mg/kg 0.1122906      mg/kg
Bush berries                        total content 2 Centre       05 - Bush berries (in-row) - CTC - pesticide             5              17.9964        mg/kg 17.8853        mg/kg
Bush berries                        total content 1 North        05 - Bush berries (in-row) - CTN - pesticide             5              37.7844        mg/kg 37.6973        mg/kg
Bush berries                        total content 3 South        05 - Bush berries (in-row) - CTS - pesticide             5              10.0547        mg/kg 9.9725076      mg/kg
Cabbage                             pore water    2 Centre       06 - Cabbage - CLC - pesticide                           5              0.22913        mg/kg 0.2185338      mg/kg
Cabbage                             pore water    1 North        06 - Cabbage - CLN - pesticide                           5              0.211262       mg/kg 0.2021885      mg/kg
Cabbage                             pore water    3 South        06 - Cabbage - CLS - pesticide                           5              0.300718       mg/kg 0.2837187      mg/kg
Cabbage                             total content 2 Centre       06 - Cabbage - CTC - pesticide                           5              10.7714        mg/kg 10.7165        mg/kg
Cabbage                             total content 1 North        06 - Cabbage - CTN - pesticide                           5              19.0308        mg/kg 18.9282        mg/kg
Cabbage                             total content 3 South        06 - Cabbage - CTS - pesticide                           5              7.44918        mg/kg 7.4031933      mg/kg
Carrots                             pore water    2 Centre       07 - Carrots - CLC - pesticide                           5              0.23481        mg/kg 0.2192811      mg/kg
Carrots                             pore water    1 North        07 - Carrots - CLN - pesticide                           5              0.209908       mg/kg 0.2035218      mg/kg
Carrots                             pore water    3 South        07 - Carrots - CLS - pesticide                           5              0.297932       mg/kg 0.2742552      mg/kg
Carrots                             total content 2 Centre       07 - Carrots - CTC - pesticide                           5              10.9855        mg/kg 10.8758        mg/kg
Carrots                             total content 1 North        07 - Carrots - CTN - pesticide                           5              18.85          mg/kg 18.7654        mg/kg
```

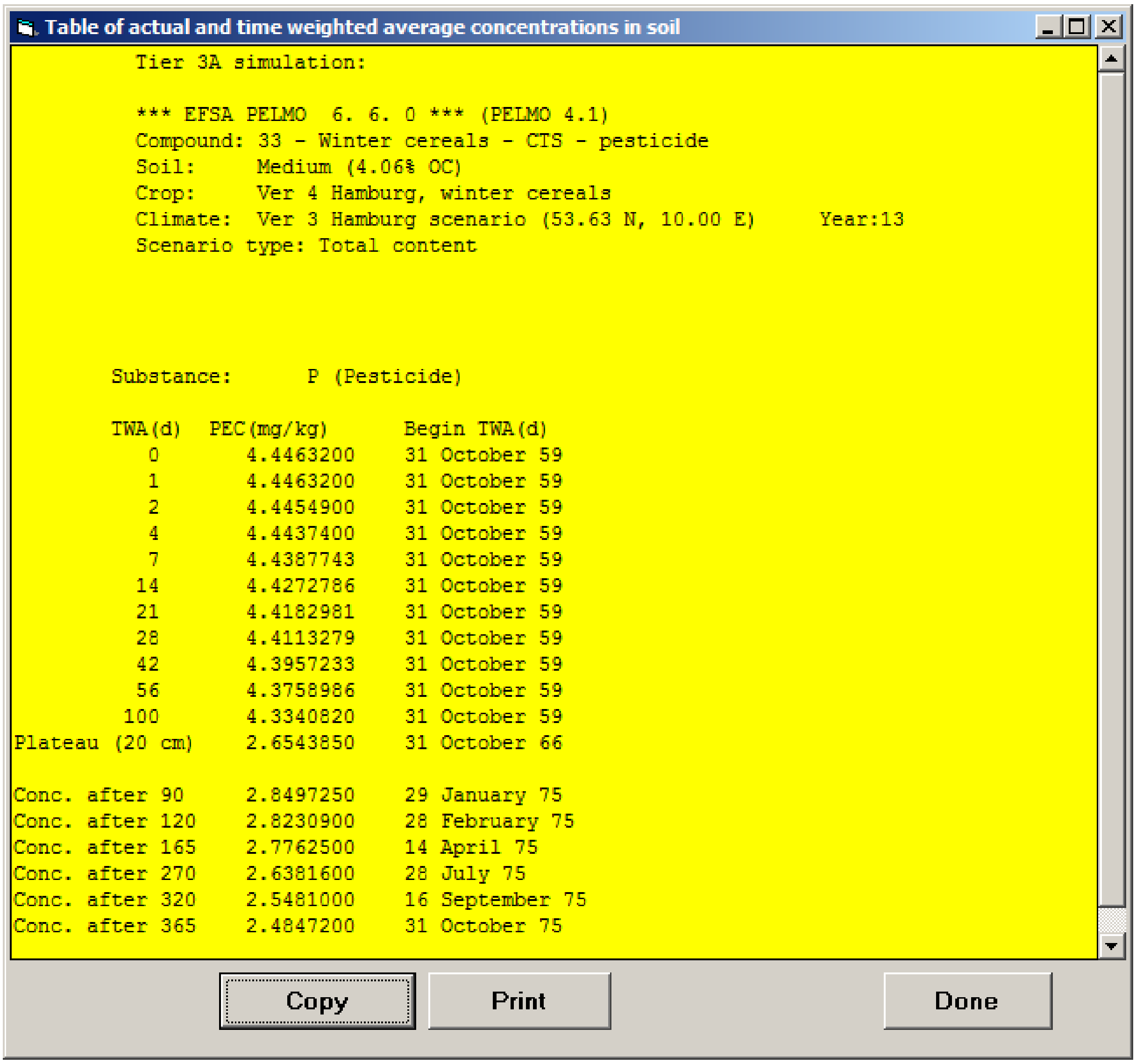
Figure 53: PELMO 5.0 Tier 3A Summary report

3.7.3.3 Results of PECsoil at Tier 3A

The button "PECsoil" in the red part of the evaluation form (see Figure 51) will present the pore water concentrations or the total content in soil of the assessed compound (see Figure 54). The results are totally based on the procedures described in EFSA (2017). The results always present actual time weighted averaged concentrations. Please consider that PELMO will always simulate the fate of all compounds defined in the. However, the results in this form are always related to the assessed compound.

All this information is also saved in ASCII-Files called "PECsoil_<*soil depth*>.plm (e.g. PEC_5.plm). The form can be used to scroll through the file, to print this information or to copy it into the clipboard.

In addition to the methodology described in EFSA (2017) PELMO also gives information about the maximum background concentration over 20 cm before the first application in a season (*i.e.,* Plateau (20 cm)). Also in addition to EFSA (2017) PELMO calculates background concentrations over 20 cm after the last application at fixed time points (90 d, 120 d, 165 d, 270 d, 320 d 365 d).

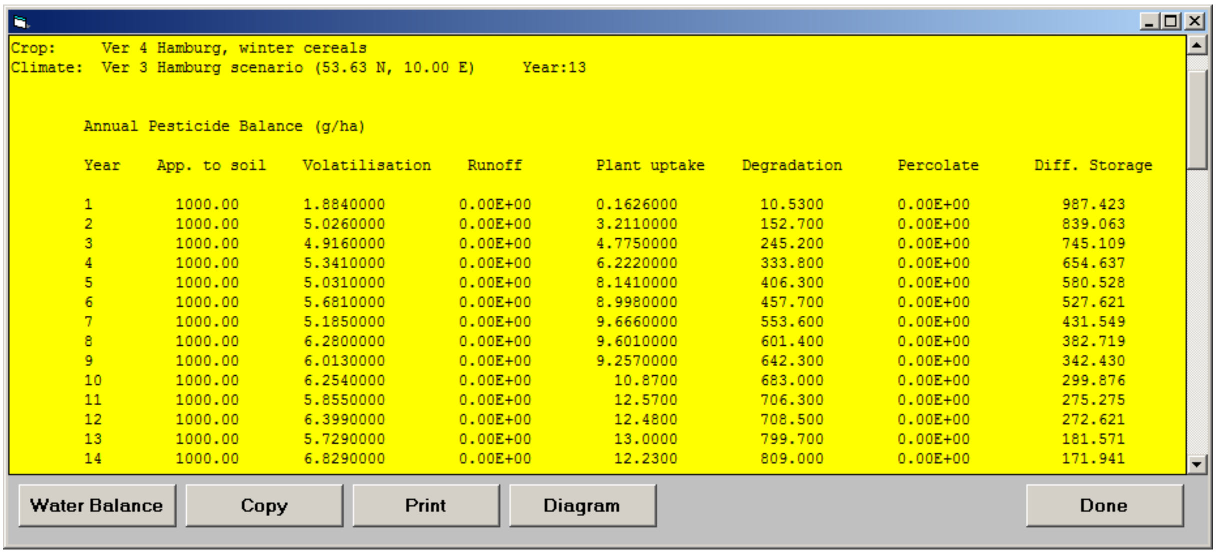


```
          Tier 3A simulation:

          *** EFSA PELMO  6. 6. 0 *** (PELMO 4.1)
          Compound: 33 - Winter cereals - CTS - pesticide
          Soil:     Medium (4.06% OC)
          Crop:     Ver 4 Hamburg, winter cereals
          Climate:  Ver 3 Hamburg scenario (53.63 N, 10.00 E)     Year:13
          Scenario type: Total content



        Substance:      P (Pesticide)

        TWA(d)  PEC(mg/kg)       Begin TWA(d)
           0       4.4463200     31 October 59
           1       4.4463200     31 October 59
           2       4.4454900     31 October 59
           4       4.4437400     31 October 59
           7       4.4387743     31 October 59
          14       4.4272786     31 October 59
          21       4.4182981     31 October 59
          28       4.4113279     31 October 59
          42       4.3957233     31 October 59
          56       4.3758986     31 October 59
         100       4.3340820     31 October 59
Plateau (20 cm)    2.6543850     31 October 66

Conc. after 90     2.8497250     29 January 75
Conc. after 120    2.8230900     28 February 75
Conc. after 165    2.7762500     14 April 75
Conc. after 270    2.6381600     28 July 75
Conc. after 320    2.5481000     16 September 75
Conc. after 365    2.4847200     31 October 75
```

Figure 54: PELMO 5.0 Tabular output of soil concentrations at EFSA Tier 3A

3.7.3.4 Mass balance

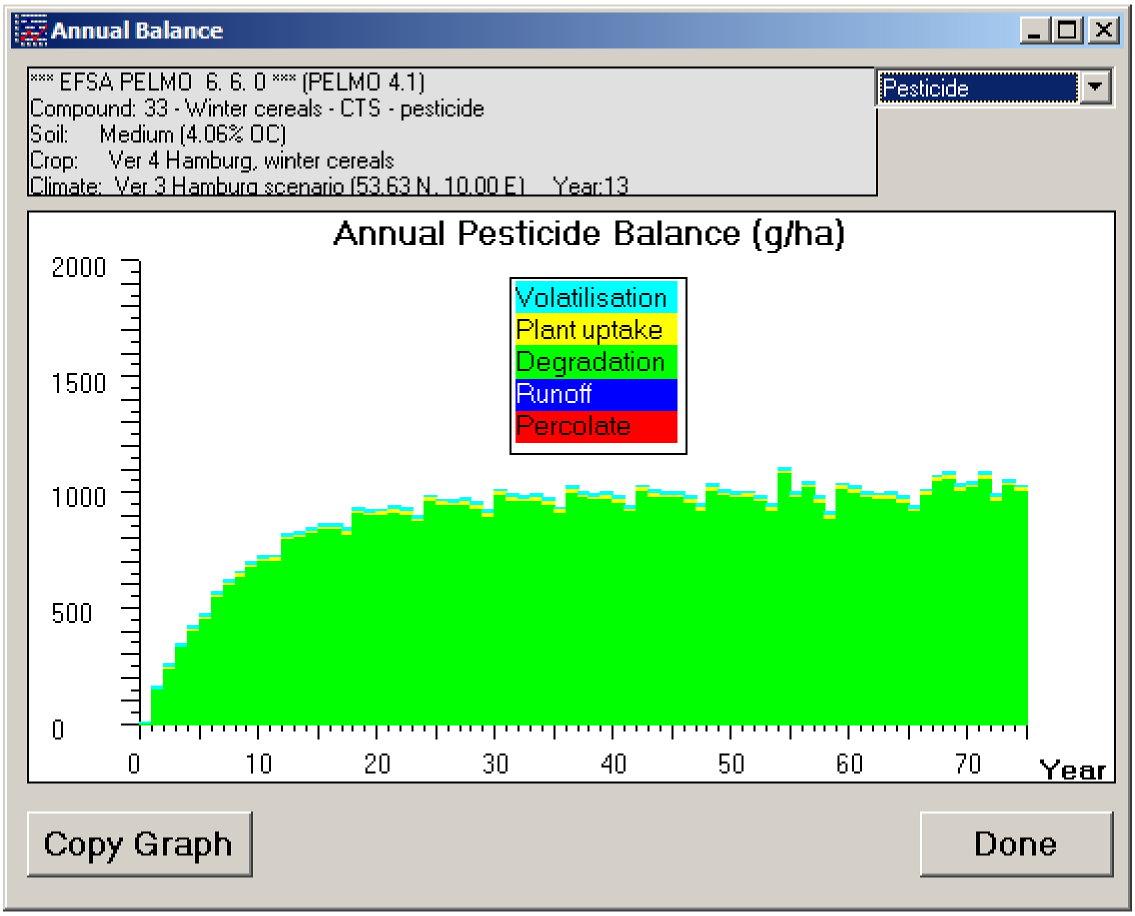
The button “Mass balance” in the red part of the evaluation form (see Figure 51) will show the annual mass balance for water, the active compound and all transformation products (see Figure 55). The table switches from hydrology to substances when using the left button. This information is also saved in ASCII-Files called “MBalance.plm” (hydrology) and “PBalance.plm” (substances). The form can be used to scroll through the file, to print this information, or to copy it into the clipboard.



```
Crop:     Ver 4 Hamburg, winter cereals
Climate:  Ver 3 Hamburg scenario (53.63 N, 10.00 E)     Year:13


      Annual Pesticide Balance (g/ha)

      Year    App. to soil    Volatilisation    Runoff       Plant uptake    Degradation      Percolate       Diff. Storage

      1         1000.00       1.8840000       0.00E+00      0.1626000       10.5300        0.00E+00          987.423
      2         1000.00       5.0260000       0.00E+00      3.2110000       152.700        0.00E+00          839.063
      3         1000.00       4.9160000       0.00E+00      4.7750000       245.200        0.00E+00          745.109
      4         1000.00       5.3410000       0.00E+00      6.2220000       333.800        0.00E+00          654.637
      5         1000.00       5.0310000       0.00E+00      8.1410000       406.300        0.00E+00          580.528
      6         1000.00       5.6810000       0.00E+00      8.9980000       457.700        0.00E+00          527.621
      7         1000.00       5.1850000       0.00E+00      9.6660000       553.600        0.00E+00          431.549
      8         1000.00       6.2800000       0.00E+00      9.6010000       601.400        0.00E+00          382.719
      9         1000.00       6.0130000       0.00E+00      9.2570000       642.300        0.00E+00          342.430
      10        1000.00       6.2540000       0.00E+00        10.8700       683.000        0.00E+00          299.876
      11        1000.00       5.8550000       0.00E+00        12.5700       706.300        0.00E+00          275.275
      12        1000.00       6.3990000       0.00E+00        12.4800       708.500        0.00E+00          272.621
      13        1000.00       5.7290000       0.00E+00        13.0000       799.700        0.00E+00          181.571
      14        1000.00       6.8290000       0.00E+00        12.2300       809.000        0.00E+00          171.941
```

Figure 55: PELMO 5.0: Tabular output of annual mass balance

The annual mass balances can be also visualised in additional diagrams. They are loaded when clicking at the button “Diagram” in Figure 56.



Annual Balance

*** EFSA PELMO 6. 6. 0 *** (PELMO 4.1)
Compound: 33 - Winter cereals - CTS - pesticide
Soil: Medium (4.06% OC)
Crop: Ver 4 Hamburg, winter cereals
Climate: Ver 3 Hamburg scenario (53.63 N, 10.00 E) Year:13

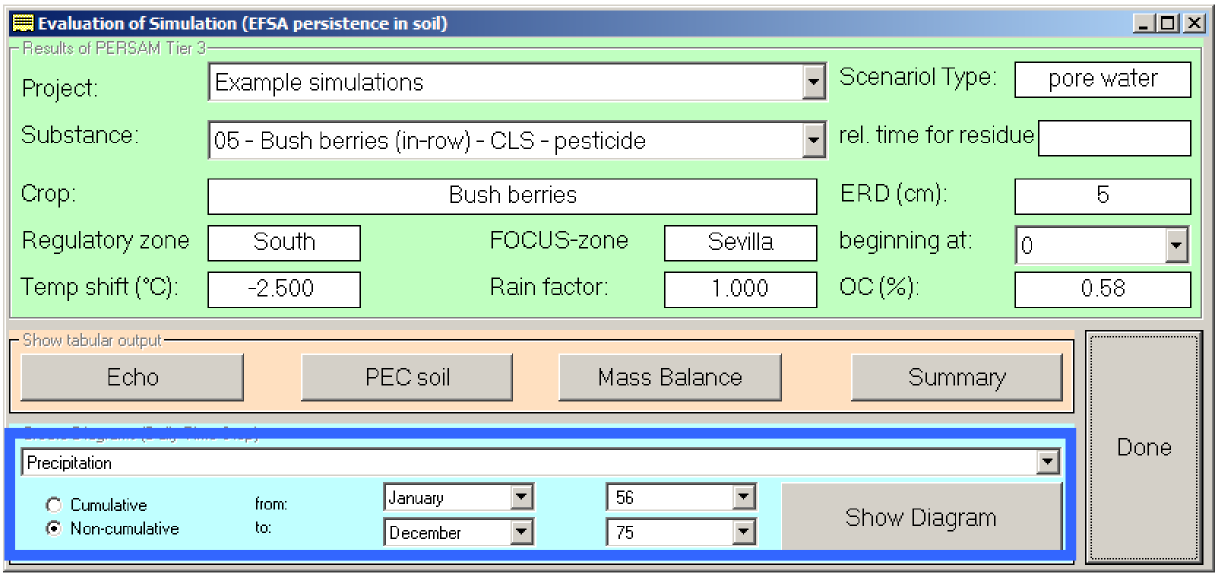
Pesticide

Figure 56: PELMO 5.0: Graphical representation of the annual mass balance

The diagram gives an overview annual mass balance (see Figure 55). It can show the annual masses for water, the active substance or transformation products. The desired output can be selected via the list box on the form.

3.7.3.5 Graphic representation of important parameters in daily resolution

Dependent on the selection made before running the simulation (see chapter 3.9) a number of diagrams can be produced in daily resolution (see the blue rectangle in Figure 57). A list of the previously selected parameters is provided in the list box. The series can be presented cumulatively or non-cumulatively. Also the period can be selected individually. The diagram is loaded when clicking at the button "show diagram" (Figure 58).



Evaluation of Simulation (EFSA persistence in soil)

Results of PERSAM Tier 3

Project: Example simulations

Substance: 05 - Bush berries (in-row) - CLS - pesticide

Crop: Bush berries

Regulatory zone: South

FOCUS-zone: Sevilla

Temp shift (°C): -2.500

Rain factor: 1.000

ScenarioI Type: pore water

rel. time for residue:

ERD (cm): 5

beginning at: 0

OC (%): 0.58

Precipitation

○ Cumulative

● Non-cumulative

from: January 56

to: December 75

Figure 57: PELMO 5.0 Analysing Tier 3A simulations using WPELMO.EXE

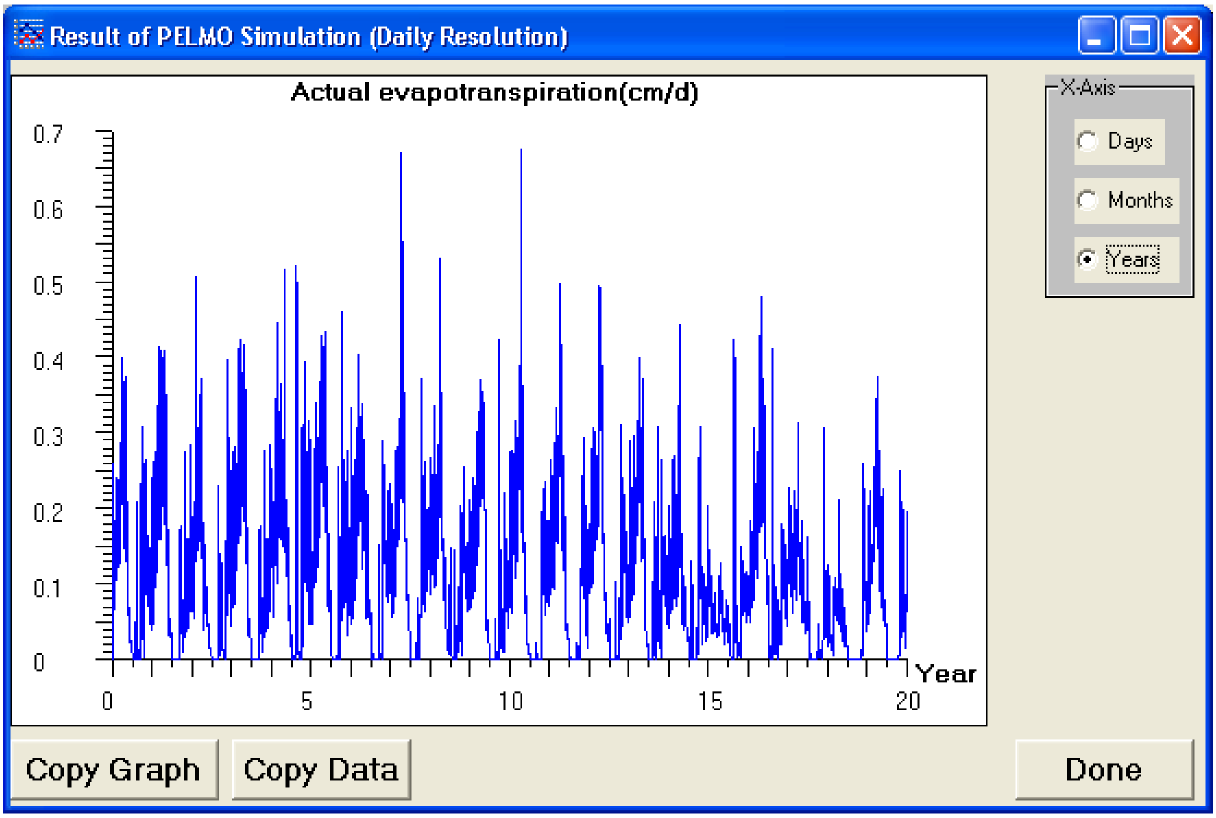


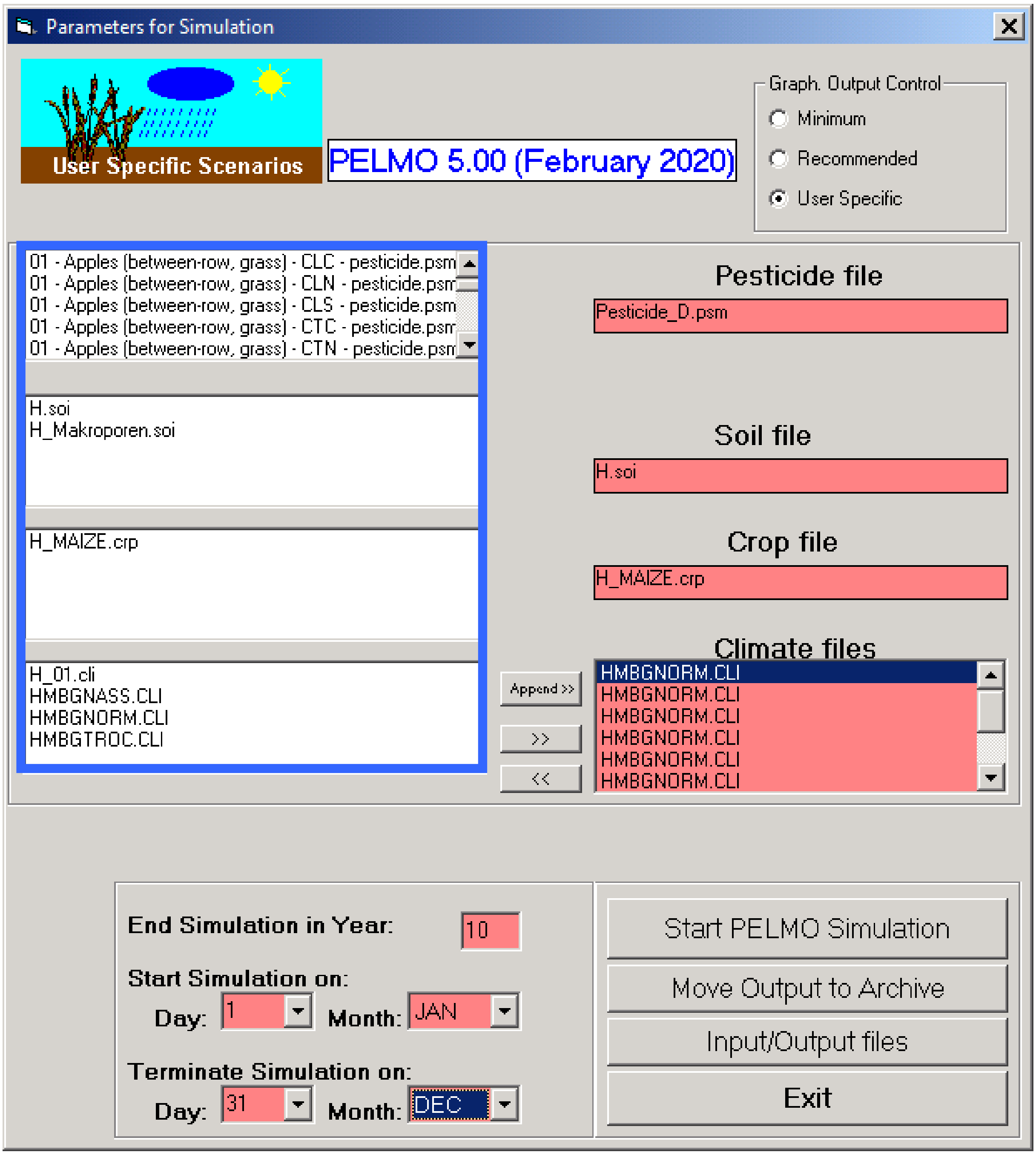
Figure 58: PELMO 5.0 Time series diagram of EFSA Tier 3A results

The unit of the x-axis can be selected (days, months, years). Either the graph as bitmap or the tabular content can be copied into the clipboard.

3.8 *Running user specific simulations*

3.8.1 Introduction

Also for individual simulations there is a special form available (see Figure 59) which can be used to combine the different type of input data for simulations. It is loaded after a click at the icon “User specific scenarios” on the main form (see Figure 10).



Graph. Output Control
○ Minimum
○ Recommended
● User Specific

01 - Apples (between-row, grass) - CLC - pesticide.psm
01 - Apples (between-row, grass) - CLN - pesticide.ps
01 - Apples (between-row, grass) - CLS - pesticide.psm
01 - Apples (between-row, grass) - CTC - pesticide.ps
01 - Apples (between-row, grass) - CTN - pesticide.ps

H.soi
H_Makroporen.soi

H_MAIZE.crp

H_01.cli
HMBGNASS.CLI
HMBGNORM.CLI
HMBGTROC.CLI

Pesticide file: Pesticide_D.psm

Soil file: H.soi

Crop file: H_MAIZE.crp

Climate files:
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI

End Simulation in Year: 10

Start Simulation on:
Day: 1 Month: JAN

Terminate Simulation on:
Day: 31 Month: DEC

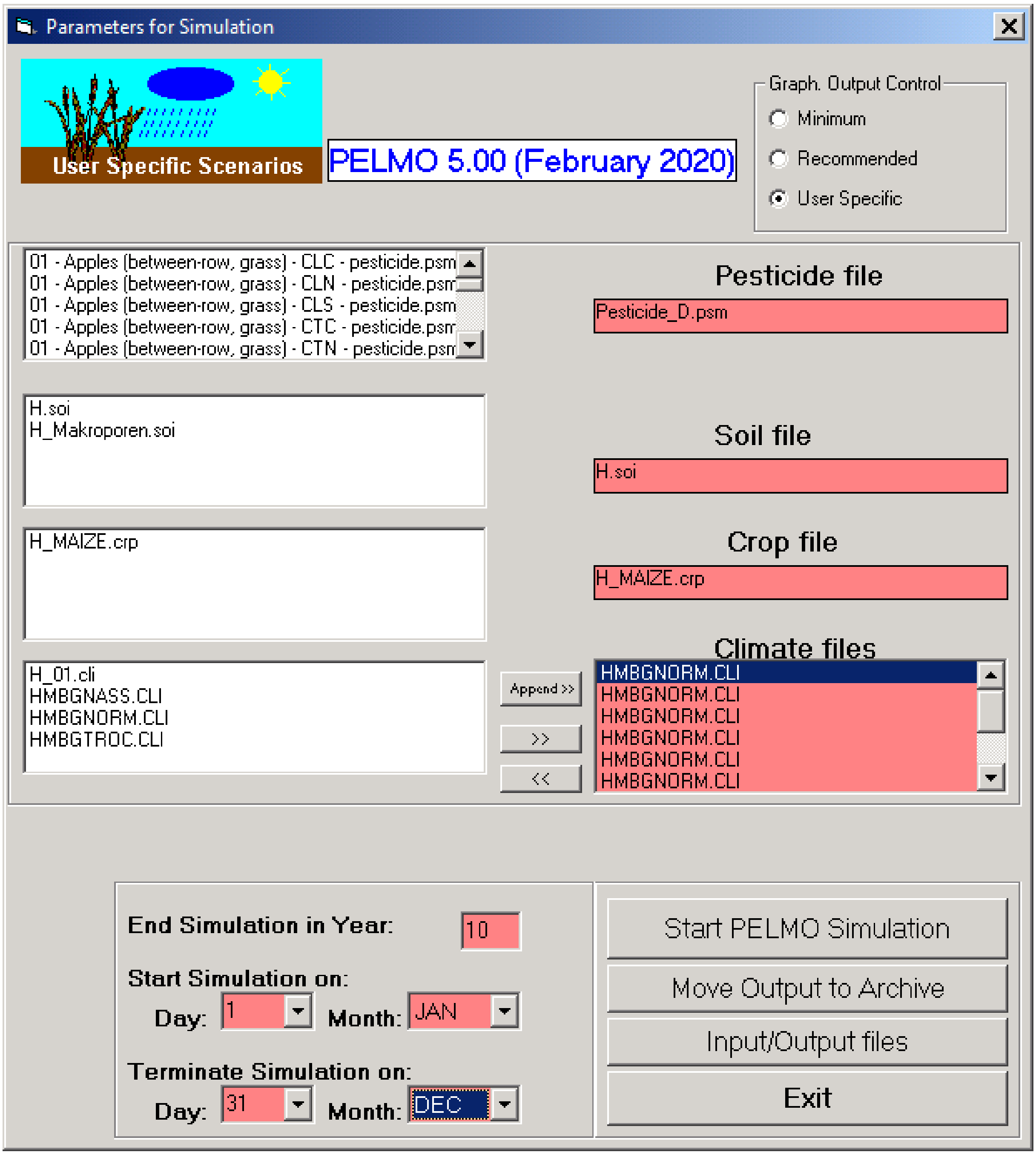
Figure 59: PELMO 5.0 Running user specific simulations

The necessary input data (pesticide data, information on soil, crop and climate) can be created by double-clicking at the input lists (blue rectangle) , soil data, crop After having created all files the user only has to select suitable input files as follows:.

1. select the pesticide input file,
2. select the soil input file to be considered,
3. select the crop input file to be considered
4. select the series of climatic data files (one for each simulation year),
5. set the simulation period (day, month, years)
6. click at “Start PELMO Simulation” to call PELMO

3.8.2 Archiving simulations

All user specific simulations are performed in the default PELMO directory. As a consequence every time PELMO runs it will replace the previous simulation. In order to save PELMO simulations the button “Move Output to Archive” (see Figure 59) can be used. After clicking at this button the backup folder can be entered and the system will create the respective directory and save the current PELMO simulation.



Graph. Output Control
○ Minimum
○ Recommended
● User Specific

01 - Apples (between-row, grass) - CLC - pesticide.psm
01 - Apples (between-row, grass) - CLN - pesticide.psm
01 - Apples (between-row, grass) - CLS - pesticide.psm
01 - Apples (between-row, grass) - CTC - pesticide.psm
01 - Apples (between-row, grass) - CTN - pesticide.psm

Pesticide file: Pesticide_D.psm

H.soi
H_Makroporen.soi

Soil file: H.soi

H_MAIZE.crp

Crop file: H_MAIZE.crp

H_01.cli
HMBGNASS.CLI
HMBGNORM.CLI
HMBGTROC.CLI

Climate files:
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI

End Simulation in Year: 10

Start Simulation on:
Day: 1 Month: JAN

Terminate Simulation on:
Day: 31 Month: DEC

Figure 60: PELMO 5.0 Running user specific simulations

3.8.3 Post processing of simulations

After a PELMO simulation successfully terminates the results can be analysed by a special module which generates all important output for pesticides and metabolites (see Figure 61). It is loaded when using the button “Input/Output files” at the user specific scenario form (Figure 59).

Usually the most recent PELMO simulation is loaded and appears at first at the form . However, by using the list boxes in the frame “Select a simulation the user can move to other simulations previously archived (see Figure 61).

To view the echo file of a simulation the respective button can be used. The other output files (extension: plm) are available when double-clicking in the respective list box. Dependent on the time resolution defined before the simulation was performed concentration in leachate at the bottom of the soil core are available either annually, monthly, or daily.

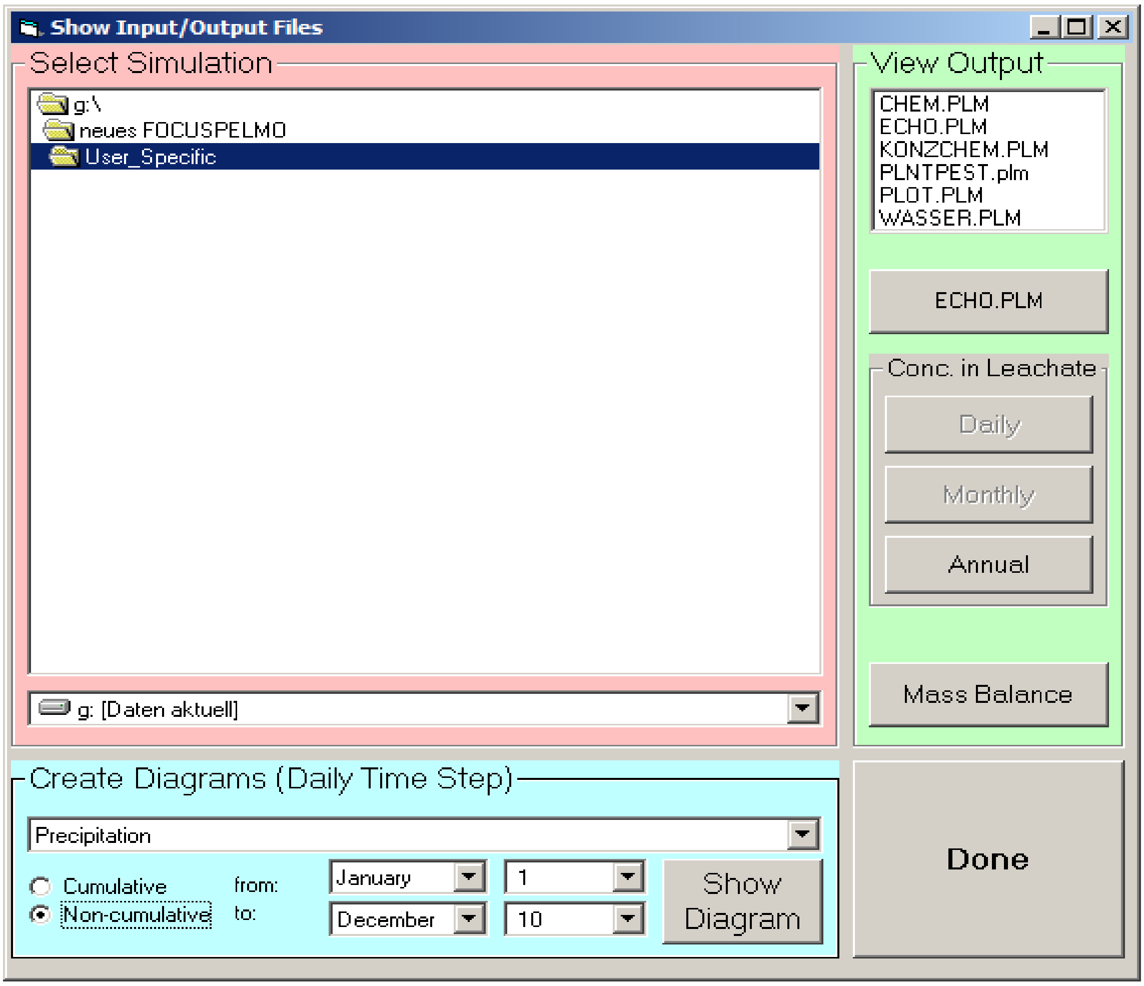


Figure 61: PELMO 5.0 Analysing user specific simulations using WPELMO.EXE

Dependent on the selection made before running the simulation (see chapter 3.9) a number of diagrams can be produced in daily resolution. A list of the previously selected parameters is provided in the list box. The series can be presented cumulatively or non-cumulatively. Also the period can be selected individually. The diagram is loaded when clicking at the button "show diagram" (Figure 62).

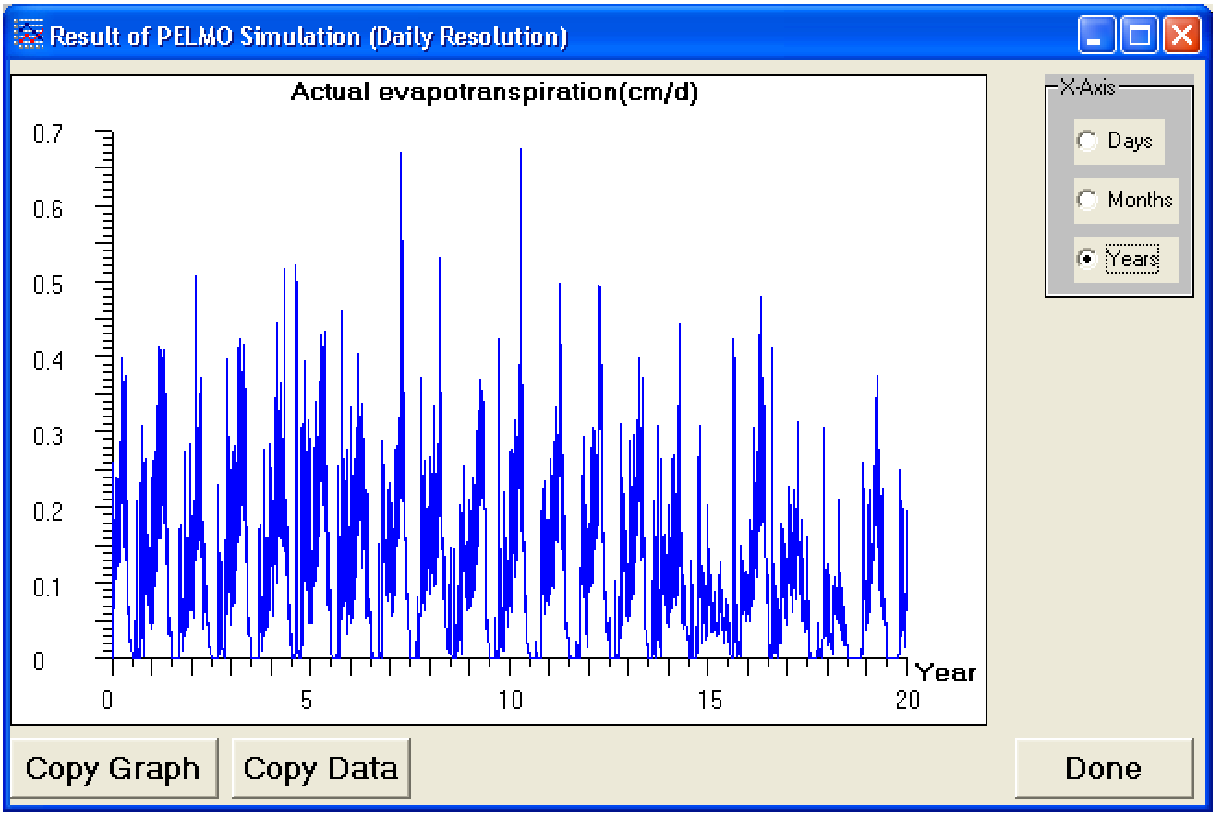
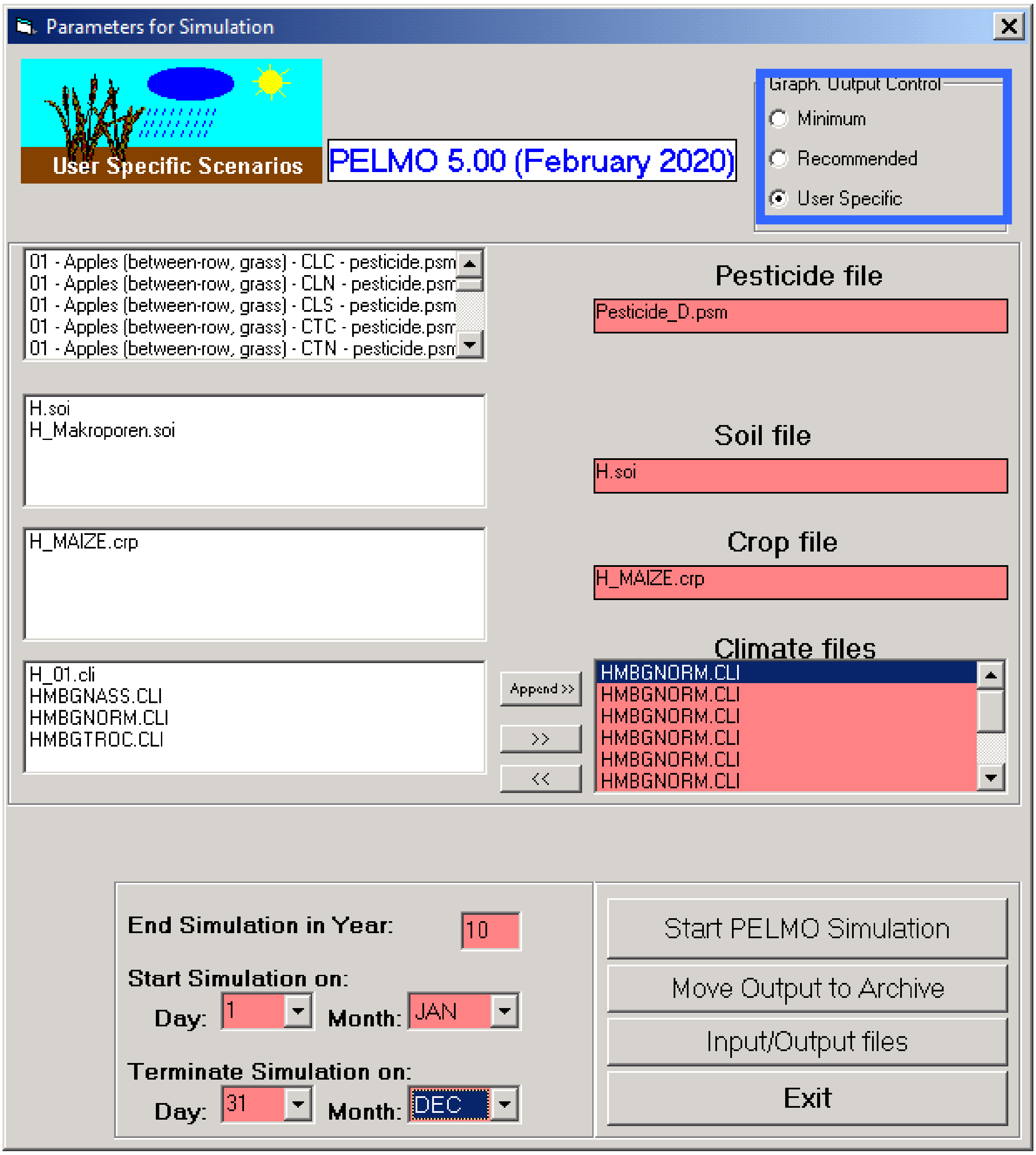


Figure 62: PELMO 5.0 Time series diagram of FOCUS results

The unit of the x-axis can be selected (days, months, years). Either the graph as bitmap or the tabular content can be copied into the clipboard.

3.9 *Preparing graphical output for post processing*

When using the field “Graph Output Control” which is available when performing all type of simulations (FOCUS, EFSA, user specific) the user can select the level of detail for simulation output before the simulations is started.



Parameters for Simulation

User Specific Scenarios

PELMO 5.00 (February 2020)

Graph. Output Control
○ Minimum
○ Recommended
● User Specific

01 - Apples (between-row, grass) - CLC - pesticide.psm
01 - Apples (between-row, grass) - CLN - pesticide.psm
01 - Apples (between-row, grass) - CLS - pesticide.psm
01 - Apples (between-row, grass) - CTC - pesticide.psm
01 - Apples (between-row, grass) - CTN - pesticide.psm

Pesticide file: Pesticide_D.psm

H.soi
H_Makroporen.soi

Soil file: H.soi

H_MAIZE.crp

Crop file: H_MAIZE.crp

H_01.cli
HMBGNASS.CLI
HMBGNORM.CLI
HMBGTROC.CLI

Climate files:
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI
HMBGNORM.CLI

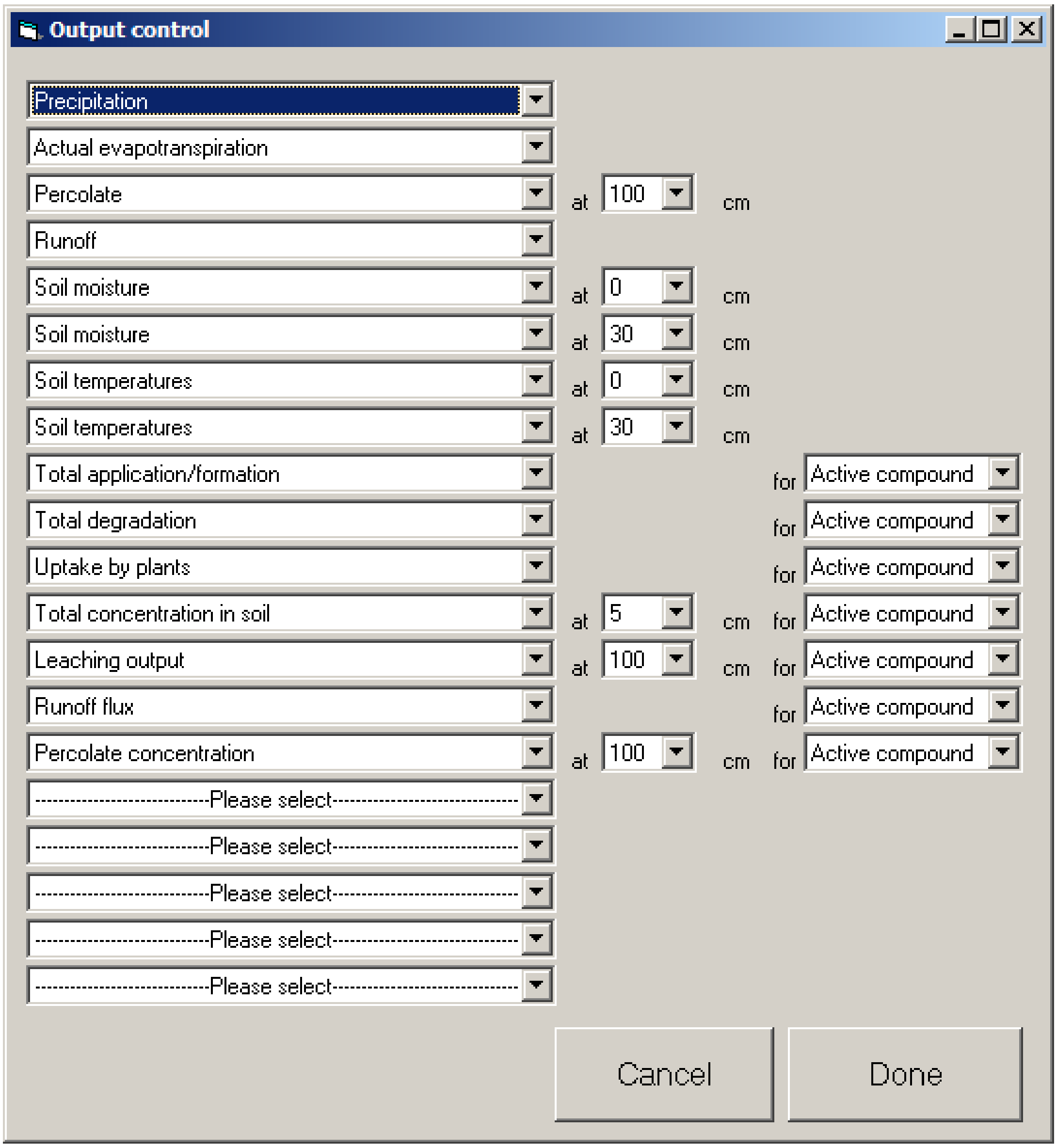
End Simulation in Year: 10

Start Simulation on:
Day: 1 Month: JAN

Terminate Simulation on:
Day: 31 Month: DEC

In the current version additional output variables were added to the list of parameters.

- Minimum output control means only for the leachate concentration at 1 m soil depth a diagram in daily resolution will be available after the simulation.
- Recommended output control will provide following output:
    - Precipitation
    - Actual evapotranspiration
    - Percolate at 1 m depth
    - Run-off
    - Soil moisture at the surface
    - Soil moisture at 30 cm
    - Soil temperatures at the surface
    - Soil temperatures at 30 cm
    - Total application
    - Total degradation for the active compound
    - Root uptake of substances by plants for the active compound
    - Total concentration in soil at 5 cm for the active compound
    - Leaching output at 1 m for the active compound
    - Run-off flux for the active compound
    - Percolate concentration at 1 m for the active compound
- “User specific output control” will open a special form where the variables for the PELMO diagrams with daily resolution can be defined for every compound simulated (see Figure 63). For each parameter the form allows (if applicable) the selection of the soil depth and/or the compound to be prepared for the daily diagrams.



Precipitation
Actual evapotranspiration
Percolate at 100 cm
Runoff
Soil moisture at 0 cm
Soil moisture at 30 cm
Soil temperatures at 0 cm
Soil temperatures at 30 cm
Total application/formation for Active compound
Total degradation for Active compound
Uptake by plants for Active compound
Total concentration in soil at 5 cm for Active compound
Leaching output at 100 cm for Active compound
Runoff flux for Active compound
Percolate concentration at 100 cm for Active compound
-----------------------------Please select--------------------------------
-----------------------------Please select--------------------------------
-----------------------------Please select--------------------------------
-----------------------------Please select--------------------------------
-----------------------------Please select--------------------------------

Figure 63: PELMO 5.0 Input sheet to define variables additional graphical output

A complete list of all parameters is presented in Table 7. If there is no depth dependency given the output is related to the whole core.

Table 7: List of variables available for daily graphical output

Parameter	Unit	Depth dependent	Substance specific
Precipitation	cm/d	no	no
Actual evapotranspiration	cm/d	no	no
Percolate	cm/d	yes	no
Run-off	cm/d	no	no
Soil loss	t/d	no	no
Soil moisture	m³/m³	yes	no
Soil temperatures	°C	yes	no
Total application	kg/ha/d	no	no
Total degradation	kg/ha/d	no	yes
Total degradation in eq. domain	kg/ha/d	no	yes
Total degradation in non-eq. domain	kg/ha/d	no	yes
Uptake by plants	kg/ha/d	no	yes
Volatilisation	kg/ha/d	no	no
Total concentration in soil	µg/cm³	yes	yes
Concentration in eq. domain	µg/cm³	yes	yes
Concentration in non-eq. domain	µg/cm³	yes	yes
Degradation	kg/ha/d	yes	yes
Degradation in equilbrium domain	kg/ha/d	yes	yes
Degradation in non-equilbrium domain	kg/ha/d	yes	yes
Leaching output	kg/ha/d	yes	yes
Run-off flux	kg/ha/d	no	yes
Erosion flux	kg/ha/d	no	yes
Percolate concentration	mg/L	yes	yes
Dissolved concentration in soil	µg/L	yes	yes
Total content in soil	mg/kg	yes	yes
Content in eq. domain	mg/kg	yes	yes
Content in non-eq. domain	mg/kg	yes	yes
Dissolved concentration in soil water	mg/L	yes	yes
Leaching input from canopy	cm/d	no	no
Pesticide wash-off from canopy	kg/ha/d	no	yes
Soil photolysis	kg/ha/d	no	yes

The same output control is available for all type of simulations (FOCUS, EFSA, user specific).

3.10 Input file description

Meteorological files (.CLI)*

Parameter and description		Value, source & comments
RECORD 1		
TITLE:	label for meteorological file	**FOCUS SCENARIO SPECIFIC**
RECORD 2 – REPEAT FOR EACH DAY OF A YEAR		**FOCUS SCENARIO SPECIFIC** Used are 9 location specific weather scenarios and 24 crop and location specific irrigated weather scenarios. hourly data are not considered for FOCUS scenarios
MD:	meteorological day	
MM:	month	
YR:	meteorological year	
PRECIP:	precipitation (cm day^{-1})	
PEVP:	pan evaporation data (cm day^{-1})	
TEMP:	14h temperature per day (°C)	
AVTEMP:	mean temperature per day (°C)	
VATEMP:	difference between min. and max. temperature per day (°C)	
RELMOI:	rel. humidity (%) – not used	
RAD:	Radiation (kJ/m²)	
HOUR:	hour (only if hourly weather data available	

Soil input files (.SOI)*

Parameter and description	Value, source & comments
RECORD 1 TITLE: label for soil title	**FOCUS SCENARIO SPECIFIC**
RECORD 2 ERFLAG: flag to select simulation of erosion.	set to 0 = **no** erosion - **FOCUS DEFINITION**
RECORD 3	Only required if ERFLAG = 1 set to 1 – **DEVELOPMENT DEFINITION**
USLEC: Universal soil loss equation cover management factor for fallow, crop and residue.	set to 0.0 = not used - **FOCUS DEFINITION** (only required if non-linear foliar application).
WFMAX: maximum dry weight of the crop at full canopy (kg m^{-2}).	set to 0.0 = not used - **FOCUS DEFINITION** (only required if non-linear foliar application).
RRPPEX: poorly exposed transformation fraction	set to 0.0 = not used - **FOCUS DEFINITION** (only required if non-linear foliar application).
	set to 0.0 = not used - **FOCUS DEFINITION** (only required if non-linear foliar application).
RRRPEX: poorly exposed penetration fraction RRVPEX: poorly exposed volatilisation fraction	set to 0.0 = not used - **FOCUS DEFINITION** (only required if non-linear foliar application).
RRWPEX: poorly exposed wash-off fraction	set to 0.0 for non-irrigated crops set to 1.0 for irrigated crops- **FOCUS DEFINITION**
IRRFLG:	
	set to 0.0 for non-irrigated crops set to 1.0 for irrigated crops- **FOCUS DEFINITION**

RECORD 4		
CORED:	total depth of soil core (cm)	**FOCUS SCENARIO SPECIFIC**
DUMMY:	dummy number	former plant uptake factor, not considered here any more, this parameter is now read in from the pesticide data file.
NCOM2	total number of simulation compartments in the soil core	**FOCUS SCENARIO SPECIFIC**
BDFLAG		set to 0 = not used
THFLAG:	field capacity and wilting point flag.	set to 0 = **the FOCUS SCENARIO SPECIFIC soil water contents are used -** Comment: another PELMO option would be to calculate field capacity and wilting point by internal pedotransfer rules using scenario specific clay and sand contents.
HSWZT:	drainage flag.	set to 0 = free draining - **FOCUS DEFINITION**
RECORD 5		
NHORIZ:	total number of horizons	**FOCUS SCENARIO SPECIFIC**
DELXFLG:	layer thickness flag	SET TO 0 = NOT USED
RECORD 6A –REPEAT 6A-6B UP TO NHORIZ		
HORIZN:	horizon number in relation to NRHORIZ.	**FOCUS SCENARIO SPECIFIC**
THKNS:	soil horizon thickness (cm).	**FOCUS SCENARIO SPECIFIC**
BD:	soil bulk density [g cm^{-3}]	**FOCUS SCENARIO SPECIFIC**
DISP:	Dispersion length (cm^{2} day^{-1})	set to 5 cm– **FOCUS DEFINITION**
THETO:	initial soil water content in the soil horizon (cm^{3} cm^{-3})	set to THEFC – **DEVELOPMENT DEFINITION**
AD: :	drainage parameter (1/d^{3})	**NOT USED FOCUS DEFINITION**
RECORD 6 B –REPEAT 6A-6B UP TO NHORIZ		
THEFC:	field capacity (cm^{3} cm^{-3}).	**FOCUS SCENARIO SPECIFIC**
THEWP:	wilting point (cm^{3} cm^{-3}).	**FOCUS SCENARIO SPECIFIC**

OC:	organic carbon content (%)	**FOCUS SCENARIO SPECIFIC**
PH:	pH value	**FOCUS SCENARIO SPECIFIC**
Biodeg:	relative biodegradation factor	depth dependent correction factor applied to the substance(s) degradation rates **FOCUS DEFINITION** 0 – 30 cm depth 1 30 – 60 cm depth 0.5 60 – 100 cm depth 0.3 > 100 cm depth 0
RECORD 7		
ROFLAG:	runoff flag	set to 0 = no runoff **–FOCUS DEFINITION**
DEPRO:	runoff depth (cm)	NOT USED (IF RUN-OFF FLAG = 0)
DOC:	dissolved organic carbon (mg/L)	**NOT USED FOCUS DEFINITION** D
DOCFLG:	doc flag	**NOT USED FOCUS DEFINITION**
DEPMA:	depth of macro pores (cm)	**NOT USED FOCUS DEFINITION**
IC:	threshould rainfall that produces macro pore flow (cm)	**NOT USED FOCUS DEFINITION**
FMAC:	fraction routed into macro pores (cm)	**NOT USED FOCUS DEFINITION**
RECORD 8		
GEOBREI:	Latitude	**FOCUS SCENARIO SPECIFIC** Comment: The geographical latitude is usually required only for calculation of the evapotranspiration by the methods of Hamon or Haude, whereas the **FOCUS DEFINITION** is to use daily pan evaporation data.

Crop input files (.SOI)*

Parameter and description	Value, source & comments
RECORD 1 TITLE: label for crop title	**FOCUS SCENARIO SPECIFIC**
RECORD 2 PFAC(0): pan factor when no crop is present used to estimate the daily potential evapotranspiration (ET) from the daily pan evaporation.	**FOCUS DEFINITION** - crop specific values are defined by the kc_year factors (see table with CN in record 9). These calibration factors reflect the soil surface and aerodynamic resistance as effective annual averages.
SFAC: snowmelt factor in cm/degrees Celsius above freezing. IPEIND: Pan evaporation flag.	set to **0.46** - **DEVELOPMENT DEFINITION** - SFAC is an empirical factor with wide variation. The value 0.46 represents an appropriate average based on data in the PRZM 3.12 manual and on Anderson, E.A.; 0.46 is also default value in PELMO 3.0
IPEIND:	set to 0 = daily pan evaporation is read from the meteorological file - **FOCUS DEFINITION**
ANETD: minimum depth for soil evaporation (cm)	**DEVELOPMENT DEFINITION** - This location specific factor is highly correlated to the climatic conditions; based on the US distribution map and the relevant 20 year average annual air temperature following values are suggested for the specific FOCUS scenarios:
INICROP: initial crop number	set to 1 = simulate initial crop - **DEVELOPMENT DEFINITION**
ISCOND: surface condition of initial crop	set to 1 = fallow **DEVELOPMENT DEFINITION**
PFAC(1): pan factor at maturation used to estimate the daily potential evapotranspiration (ET) from the daily pan evaporation.	not used for FOCUS simulations
PFAC(2): pan factor at senescence used to estimate the daily potential evapotranspiration (ET) from the daily pan evaporation.	not used for FOCUS simulations

RECORD 3		
NDC:	number of different crops in the simulation.	set to 1 = only **one** crop - **FOCUS DEFINITION**
TILFLG	tillage flag.	set to 0 0 no tillage
RECORD 4 – REPEAT UP TO NDC		
ICNCN:	crop number of the different crop.	set to 1 = the crop used - **FOCUS DEFINITION**
CINTCP:	maximum interception storage of the crop (cm).	set to zero = no rainfall interception - **FOCUS DEFINITION**
AMXDR:	maximum rooting depth of the crop (cm).	**FOCUS SCENARIO SPECIFIC**
LAIMAX:	maximum leaf area index of the crop.	**FOCUS SCENARIO SPECIFIC** -
ICNAH:	surface condition of the crop after harvest date (fallow, cropping, residue).	set to 3 = residue **DEVELOPMENT DEFINITION**
CN:	runoff curve numbers of antecedent moisture condition II for fallow, cropping, residue (3 values).	Runoff is calculated by a modification of the USDA Soil Conservation Service curve number approach (Haith *et al*., 1979). The curve numbers were selected based on two definitions: 1) **SCS hydraulic Soil Group:** The SCS group was chosen for Piacenza to be **A**, Hamburg to be **B** and for all the rest locations to be **C** - **FOCUS DEFINITION** 2) **Curve Numbers:** Crop and soil specific CN are defined corresponding to values of PELMO 3.0, the original USDA definition and the PRZM 3.12 manual. – **DEVELOPMENT DEFINITION**

SCS soil group:	**A**	**B**	**C**	**D**	HTMAX	PFAC
- fallow + residue	77	86	91	94	-	1.00
– apples (orchards)	36	60	73	79	250	0.99
– grass (+alfalfa)	30	58	71	78	40	1.00
– potatoes	62	83	89	93	100	0.94
– sugar beet	58	72	81	85	40	0.93
– winter cereals	54	70	80	85	100	0.84
- beans (field+vegetable)	67	78	85	89	150	0.89
– bush berries	36	60	73	79	130	1.00
– cabbage	58	72	81	85	30	0.97
– carrots	58	72	81	85	40	0.96
– citrus	36	60	73	79	250	0.73
– cotton	67	78	85	89	120	0.95
– linseed	54	70	80	85	150	0.84
– maize	62	83	89	93	250	0.94
– oil seed rape (sum)	54	70	80	85	140	0.93
– oil seed rape (win)	54	70	80	85	140	0.78
– onions	58	72	81	85	60	0.91
– peas (animals)	67	78	85	89	100	0.96
– soybean	67	78	85	89	170	0.92
– spring cereals	54	70	80	85	110	0.92
– strawberries	58	72	81	85	40	1.00
– sunflower	62	83	89	93	150	0.86
– tobacco	67	78	85	89	250	0.98
– tomatoes	62	74	81	86	110	0.97
– vines	45	62	73	79	170	0.89

For all perennial crops (alfalfa, apples, bushberries citrus, grass, strawberries, vines) the same CN are used for fallow and residue!

RRPPEX:	relative process rate for poorly exposed pesticides deposits compared to well exposed, process penetration into leaves	set to 0.2 = the crop used - DEVELOPMENT DEFINITION
RRRPEX:	relative process rate for poorly exposed pesticides deposits compared to well exposed, process photo-degradation on leaves	set to 0.2 = the crop used - DEVELOPMENT DEFINITION
RRVPEX:	relative process rate for poorly exposed pesticides deposits compared to well exposed, process volatilisation from leaves	set to 0.2 = the crop used - DEVELOPMENT DEFINITION
RRWPEX:	relative process rate for poorly exposed pesticides deposits compared to well exposed, process wash-off from leaves	set to 0.2 = the crop used - DEVELOPMENT DEFINITION
IRRFLG:	irrigation flag	0: no irrigation, 1: sprinkler 2: drip irrigation
PEREN:	perennial crop	1: no 2: yes

PFAC(1): pan factor at maturation used to estimate the daily potential evapotranspiration (ET) from the daily pan evaporation.	**FOCUS DEFINITION** - crop specific values are defined by the kc_year factors (see table with CN in record 9). These calibration factors reflect the soil surface and aerodynamic resistance as effective annual averages.
PFAC(2): pan factor at senescence used to estimate the daily potential evapotranspiration (ET) from the daily pan evaporation.	**FOCUS DEFINITION** - crop specific values are defined by the kc_year factors (see table with CN in record 9). These calibration factors reflect the soil surface and aerodynamic resistance as effective annual averages.
BEER: Beer's law extinction coefficient	set to 0.39 **FOCUS DEFINITION** -
LAIMIN: minimm LAI	**FOCUS SCENARIO SPECIFIC**
SPRINGPT: irrigation flag	**FOCUS SCENARIO SPECIFIC**
RECORD 5	
NCPDS: number of cropping periods.	set to 66 (= longest possible simulation period) - **FOCUS DEFINITION**
RECORD 6 - REPEAT UP TO NCPDS	
E_MMDDYY: crop emergence date (month/day/year).	**FOCUS SCENARIO SPECIFIC**
M_MMDDYY: crop maturation date.	**FOCUS SCENARIO SPECIFIC**
H_MMDDYY: crop harvest date.	**FOCUS SCENARIO SPECIFIC**
INCROP: crop number associated with NDC	set to 1 (only one crop) - **FOCUS DEFINITION**
H_MMDDYY: crop senescence date.	**FOCUS SCENARIO SPECIFIC**
RECORD 5	
NCPDS: number of mechanical treatments	Set to 0
RECORD 6 - REPEAT UP TO NCPDS	
E_MMDDYY: crop emergence date (month/day/year).	Not used
TILDEPTH	Not used

Substance file (.PSM)*

Parameter and description	Value, source & comments
Comment: Text and / or lines in the substance file that are given in brackets (< >) are comments for easier understanding of the file structure and mark the beginning or end of a parameter section. These lines should not be changed. The compound parameters are described here only for the parent compound. In principle, all processes except from volatilisation are taken into account also for each metabolite. Therefore, for each metabolite to be simulated, a similar set of parameters needs to be included, leaving out only the volatilisation data.	
COMMENT	
`CTITLE`: label for substance	**USER INPUT**
SOIL HORIZONS	
NHORIZ: total number of soil horizons	set to 0 = not used - **DEVELOPMENT DEFINITION** Comment: This parameter is required if depth dependent biodegradation factors are specified in the substance file instead of the scenario file. The parameter has then to be set to the scenario specific number of horizons.
NUMBER OF LOCATIONS	
N_LOC: number of locations for which applications will be defined (1-10)	**FOCUS SCENARIO SPECIFIC / USER INPUT**
DUMMY:	not used
REL_ABS_APP:	0: absolute application dates 9: relative application dates
APPLICATIONS - REPEAT UP TO N_LOC	
NAPS: total number of substance applications occurring at different dates (1 – 200).	**FOCUS SCENARIO SPECIFIC / USER INPUT**

APPLICATIONS – REPEAT UP TO NAPS (IF ABSOLUTE APPLICATIONS ARE SELECTED)		
APD:	Day of the month of application	**USER INPUT**
APM:	Month of application	**USER INPUT**
IAPYR:	Year of application	**USER INPUT**
TAPP:	Total application rate (kg ha^{-1})	**USER INPUT**
UP_DEPI:	Upper Depth of incorporation (cm)	**USER INPUT**
DEPI:	Lower Depth of incorporation (cm)	**USER INPUT**
COVAPP:	crop interception during application (%)	**NOT USED FOR FOCUS SIMULATIONS**
FRPEC:	fraction of poorly exposed pesticide	**NOT USED FOR FOCUS SIMULATIONS**
APT:	application hour	**NOT USED FOR FOCUS SIMULATIONS**
APPLICATIONS – REPEAT UP TO NAPS (IF RELATIVE APPLICATIONS ARE SELECTED)		
APD:	Day relative to crop status	**USER INPUT**
APM:	crop development type (emergence, harvest)	**USER INPUT**
IAPYR:	Year of application	**USER INPUT**
TAPP:	Total application rate (kg ha^{-1})	**USER INPUT**
UP_DEPI:	Upper Depth of incorporation (cm)	**USER INPUT**
DEPI:	Lower Depth of incorporation (cm)	**NOT USED FOR FOCUS SIMULATIONS**
COVAPP:	crop interception during application (%)	**NOT USED FOR FOCUS SIMULATIONS**
FRPEC:	fraction of poorly exposed pesticide	**NOT USED FOR FOCUS SIMULATIONS**
APT:	application hour	
APPLICATION MODE		
FAM:	Substance application model	**USER INPUT** Selectable chemical application methods are: **1** = application to soil only **2** = foliar application using the linear model **3** = non-linear foliar application using exponential filtration model **4** = application to the foliar, manual crop interception.

FOLIAR APPLICATION PARAMETERS (ONLY IF FAM = 2 OR 3)		
PLDKRT:	Decay rate on the plant foliate (days^{-1})	Not used for FOCUS scenarios
FEXTRC:	Foliar extraction coefficient for substance washoff per cm of precipitation	Not used for FOCUS scenarios
FILTRA:	Filtration parameter. Only required for exponential model (FAM = 3).	Not used for FOCUS scenarios
FILTRA:	Filtration parameter. Only required for exponential model (FAM = 3).	Not used for FOCUS scenarios
FPENET:	Penetration rate into the plant foliate (day^{-1}) FPENET	Not used for FOCUS scenarios
PHRATE:	Photodegardation rate (1/d)	Not used for FOCUS scenarios
RADREF:	reference irradiance (W/m²)	Not used for FOCUS scenarios
DLAM:	Laminar layer for volatilisation from foliate (W/m²)	Not used for FOCUS scenarios
FLAGS		
VAPFLG:	Henry's constant flag	**USER INPUT** **0** = Henry's constant input by user **1** = Henry's constant calculated
KDFLAG:	K_D flag	**USER INPUT** **0** = K_D input by user **1** = K_D calculated from K_{OC}

VOLATILISATION 2 RECORDS, ONE FOR EACH TEMPERATURE		
HENRYK:	normalised Henry's law constant of the active substance (dimensionless).	Comment: Henry's constant **H** is a ratio of a chemical's vapour pressure to its solubility. It represents the equilibrium between the vapour and solution phases.): $HENRYK = H / (R*T) = P*M / (C*R*T)$ P = vapour pressure (Pa) - **USER INPUT** M = mol weight (g mole^{-1}) - **USER INPUT** C = water solubility (mg L^{-1}) - **USER INPUT** R = gas constant = 8.3144 J K^{-1} mole^{-1} T = absolute temperature (K)
SOLUB:	Solubility in water (mg L^{-1})	**USER INPUT**
MOLMAS:	Molar mass (g mol^{-1})	**USER INPUT**
VAPPRE:	Vapour pressure (Pa)	required for calculation of Henry's constant - **USER INPUT**
DAIR:	molecular diffusion coefficient for the substance(s) in the air (cm^2 sec^{-1})	required for calculation of Henry's constant - **USER INPUT**
VOLGRE:	depth for volatilisation (cm)	set to 0.1 cm – **FOCUS DEFINITION**
T_VOL:	Related Temperature (°C)	**USER INPUT**
PLANT UPTAKE		
UPTKF:	plant uptake factor (between 0.000 and 1.0; describes uptake as a fraction of transpiration* dissolved phase concentration)	**USER INPUT** set to 0.5 for systemic compounds (default) set to 0 = **no** plant uptake for other compounds Other values not to be used for TIER 1 modelling!
DEGRADATION - REPEAT FOR METABOLISATION PATHS A1 – D1 AND BOUND RESIDUES / CO2		
DKRATE:	degradation rate constant (day^{-1})	**USER INPUT -** Can also be entered as a DEGT50 value
TEMP0:	reference temperature for the degradation rate constant (°C)	**USER INPUT**
Q10:	Q10-factor for degradation rate increase when temperature increases by 10°C	**USER INPUT** default = 2.2 - **FOCUS DEFINITION**
ABSFEU:	absolute reference moisture content during the degradation studies (%Vol)	**USER INPUT**

FELFEU:	relative reference moisture content during the degradation studies (% of FC (field capacity))	**USER INPUT** Comment: either absolute or relative soil moisture has to be specified, the other parameter should be set to 0
FEUEXP:	Exponent for the moisture dependent correction of the degradation rate constant (moisture relationship according to WALKER)	**USER INPUT** default = 0.7 – **FOCUS DEFINITION**
FLAG		
DEGFLAG:	flag controlling depth dependent degradation	**USER INPUT** 0: degradation according to degradation factors in the scenario file 1: degradation constant with depth 2: degradation according to individual factors in the pesticide data file For TIER 1 modelling the flag should be set to 0.
ADSORPTION (IF KDFLAG = 1)		
KOC:	K_{OC} value (ml g^{-1})	**USER INPUT**
FRNEXKOC:	Freundlich exponent 1/n (dimensionless)	**USER INPUT**
PH_KOC:	pH value	**USER INPUT** default = 7
PKA:	pKA value	**USER INPUT** default = 20, ie in practice not used
FRNMIN:	lower limit concentration for the non-linear sorption according to Freundlich (µg L^{-1})	**USER INPUT** default = 10^{-20} µg L^{-1}
ALTERN:	annual increase of adsorption (%)	**USER INPUT** default = 0 (no increase of sorption with time)
K_DOC:	Equilibrium constant for DOC (L/kg)	**not used for FOCUS simulations**
KOC_MOI:	Increase when soil is air dried (-)	**USER INPUT** default = 0 (no increase of sorption with mositure)
KOC2:	second K_{OC} value at a different pH (ml g^{-1})	**USER INPUT**
PHKOC2:	pH value related to the second KOC	**USER INPUT**
FNEQ:	fraction of non-equilibrium sites	**USER INPUT**
KDES	desorption rate (1/d)	**USER INPUT**

DEPTH DEPENDENT SORPTION AND DEGRADATION (ONLY IF DEGFLAG=2) – REPEAT FOR EACH SOIL HORIZON		
KD :	K_D value (ml g^{-1})	**USER INPUT** (only considered by PELMO if kdflag = 0)
FRNEXP:	Freundlich exponent 1/n (dimensionless)	**USER INPUT** (only considered by PELMO if kdflag = 0)
DEG(1):	depth dependent correction of degradation rate for metabolism path A1	**USER INPUT**
DEG(2):	depth dependent correction of degradation rate for metabolism path B1	**USER INPUT**
DEG(3):	depth dependent correction of degradation rate for metabolism path C1	**USER INPUT**
DEG(4):	depth dependent correction of degradation rate for metabolism path D1	**USER INPUT**
DEG(5):	depth dependent correction of degradation rate for metabolism path BR/CO2	**USER INPUT** Comment: the depth dependent correction of degradation can also be specified in the scenario file. According to **FOCUS DEFINITION** the depth dependent correction factors are 0 – 30 cm depth 1 30 – 60 cm depth 0.5 60 – 100 cm depth 0.3 > 100 cm depth 0

Control file PELMO.INP

Parameter and description	Value, source & comments
RECORD 1	
IYEAR: number of years of simulation period	26, 46, or 66 years - **FOCUS DEFINITION**
ISDAY: start day of simulation	1 – **DEVELOPMENT DEFINITION**
ISMON: start month of simulation	1 - **DEVELOPMENT DEFINITION**
IEDAY: end day of simulation	31 - **DEVELOPMENT DEFINITION**
IEMON: end month of simulation	12 - **DEVELOPMENT DEFINITION**
RECORD 2	
APPLIK: scenario parameter file name	**USER INPUT, FOCUS DEFINITION**
RECORD 3	
CHEM: substance parameter file name	**USER INPUT**
RECORD 4 - REPEAT UP TO (NUMBER OF SIMULATION YEARS)	
KLIMA: climate file name	**USER INPUT, FOCUS DEFINITION**
RECORD 13	
NPLOTS: Number of time series to be written to plotting file	22 **- DEVELOPMENT DEFINITION**
RECORD 14 – REPEAT UP TO NPLTOTS	
PLNAME: Identifier of time series MODE: Plotting mode IARG: Argument of variable identified in PLNAME CONST: Constant used for unit conversion	**DEVELOPMENT DEFINITION** Comment: The time series identified here are requirements for the graphical output and analysis within the Graphical User Interface. They cannot be changed.

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Annex A:
Implementation of kinetic sorption into PELMO

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1 Summary

The appendix describes the implementation of kinetic sorption into PELMO, the Pesticide Leaching Model, which is used in European registration to calculate the leaching potential of pesticides (FOCUS 2000).

FOCUS (2009) describes three methods to simulate kinetic sorption in soil. One of these methods is the STRECK-approach which was recently added to the leaching model PRZM. The same method has been now also implemented in PELMO. However, automatic transformation of input parameters in the PELMO shell makes it possible to consider kinetic sorption parameters also according to the alternative approach realised in the leaching model PEARL and also described by FOCUS (2007).

In contrast to the PEARL methodology of kinetic sorption also degradation processes at non-equilibrium sites were considered in the new PELMO routines. These additional processes follow 1st order kinetics with a special rate constant, but same moisture, depth and temperature dependency as in the traditional equilibrium domain.

All input and output routines in PELMO were adapted to process the new parameters. A couple of further subroutines modules in PELMO were extended with additional code to perform the new calculations.

The FOCUS PELMO shell (wpelmo.exe) was also extended to cover the new parameters. Within the shell it is possible to transfer PEARL into Streck-parameter setting (and *vice versa*). In the new version of the shell it is furthermore possible to create daily diagrams to visualise concentration and degradation in the non-equilibrium domain.

Non-equilibrium sorption was implemented successfully in PELMO as demonstrated by the excellent agreement with respective PEARL-simulations performed in several test runs.

Simulations with example pesticide FOCUS D and annual applications in winter cereals showed that the new kinetic sorption module usually leads to a reduction of annual concentrations in the percolate. However, in same cases also higher concentrations were simulated.

2 Introduction

FOCUS PELMO is one of four leaching computer models officially used within the EU pesticide registration (FOCUS 2000, Jene 1998, Klein 1995). The previous version of PELMO assumes that sorption in soil can be totally described by equilibrium conditions using the Freundlich equation. However, long-term sorption experiments showed that these processes do quite often not follow this theory.

Therefore, in PEARL and MACRO, two other FOCUS-leaching models, additional routines have been implemented that are able to describe this non-equilibrium or kinetic sorption process. The realisation in these models is based on a two-region-model assuming that the equilibrium sorption of a substance can be separated from non-equilibrium type sorption by assuming two different types of sorption sites in soil.

Generally, additional parameters have to be defined to describe the sorption isotherm at the non-equilibrium sites, and parameters that describe the adsorption and desorption rates between the site and possibly and additional degradation rate at the non-equilibrium sites.

In the year 2004 a new FOCUS-groundwater scenario group was established. A major task of this group was the harmonisation of the current FOCUS-models. This group classified non-equilibrium sorption in soil as one possibility of improved modelling with refined parameterisation at higher tier level. Therefore, this process was also implemented in FOCUS PELMO.

Recently also FOCUS PRZM has been extended in order to consider kinetic sorption. To achieve maximum harmonisation between the FOCUS models principally the same algorithm was used in PELMO as in PRZM.

This implementation was done based on the new version of PELMO that has been modified according to the suggestions of the new FOCUS GW scenario group (e.g. dispersion length, no-run-off-option in first tier, depth-dependent compartment sizes).

3 Methodology

4.1 Introduction

A popular model for dealing with sorption kinetics is the two-site/two-region model (Van Genuchten and Wagenet, 1989; Streck et al., 1995), which separates the soil sorption sites in equilibrium and non-equilibrium sites. The basis for this simplification is that sorption sites reacting at time scales ranging from minutes to a day or two are close enough to equilibrium when assessing pesticide leaching to ground water. The two-site sorption and degradation kinetics model assumes two soil fractions (sites) coexisting in a soil representative elementary volume, with one adsorbing chemicals instantaneously and the other time-dependently (FOCUS 2009).

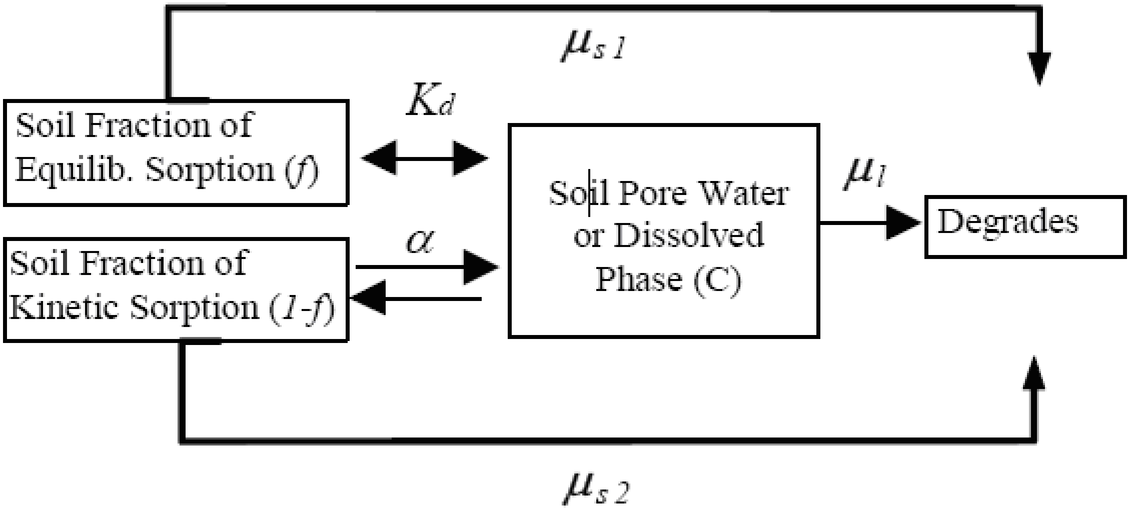

Figure A 1: Two domain model to describe kinetic sorption

FOCUS (2009) describe three methods to simulate kinetic sorption in soil

- The PEARL-approach
- The Streck –approach (implemented in PRZM)
- The MACRO-approach

The models are different with respect to the definition of the total concentration sorbed. However, as shown by FOCUS (2009) the models are mathematically identical, because they describe the same process and the parameters derived using one of the models can be translated into parameters of the other. In this project the STRECK-model was implemented in the simulation model PELMO, but automatic transformation of input parameters in the PELMO shell makes it possible to consider kinetic sorption parameters according to the PEARL approach.

Degradation processes at non-equilibrium sites follow 1st order kinetics with a special rate constant, but same moisture, depth and temperature dependency as at the traditional equilibrium sites. It is, of course, possible to run simulations without this additional degradation process in the non-equilibrium domain.

The so far mentioned extensions refer to the key procedure SLPEST. Within this routine it is calculated, how the concentrations of parent and metabolites change within a time step (usually 1 day). Additional modifications were made in following subroutines:

READIN: Input of the new parameters,
ECHO: Output of the new parameters,
OUTPST: Modification of tables writing the file chem.plm which contains the daily concentration at the non-equilibrium sites and the related fluxes
OUTTSR: time dependent output of the movement of chemicals between equilibrium and non-equilibrium sites (written into plot.plm),
MASBAL: checking the mass balance each day
PESTAP: organising pesticide application to the crop or the soil surface,
INITL: initialising of all variables
MAIN: updating all storage variables at the end of the day
TRANSFORM_NEQ new function to calculate dynamic transformation rates in the non-equilibrium domain
SOURC_NEQ new function to calculate metabolite formation in the non-equilibrium domain
VERTEIL: redistribution of compound masses between soil water and soil matrix after a new application has been performed

4.2 New Variables in PELMO

To consider the non-kinetic sorption new parameters were defined in PELMO. An overview about these new variables is given in Table A 1.

Table A 1: New Variables defined in PELMO to simulate kinetic sorption

Variable	Unit	FORTRAN Dimension	Occurence	Meaning
prx1	-	-	SLPEST	parameter R_1 in eq. 15
prz	-	-	SLPEST	parameter R in eq. 16
pomegax	day^{-1}	-	SLPEST	parameter ω in eq. 13
pgammax	day^{-1}	-	SLPEST	parameter γ in eq. 14
pmux	day^{-1}	-	SLPEST	parameter μ_e in eq. 12
pbx	day^{-1}	-	SLPEST	parameter b in eq. 10
pcx	day^{-2}	-	SLPEST	parameter c in eq. 11
plambdax1	day^{-1}	-	SLPEST	parameter λ_1 in eq. 8
plambdax2	day^{-1}	-	SLPEST	parameter λ_2 in eq. 9
p1c	day^{-1}	-	SLPEST	parameter p_{1c} in eq. 6a
p2c	µg/g	-	SLPEST	parameter p_{2c} in eq. 6b
p1s	-	-	SLPEST	parameter p_{1c} in eq. 7a
p2s	day^{-1}	-	SLPEST	parameter p_{2c} in eq. 7b
s2	µg/g	(MET,COMP)	SLPEST, MAIN MASBAL, OUTPST OUTTSR	concentration in the non-equilibrium domain
kdes	day^{-1}	(MET,COMP)	SLPEST	1st order desorption rate in the non-equilibrium domain
dsrate*	day^{-1}	(MET,COMP)	SLPEST	1st order degradation rate for sorbed pesticide fraction in the equilibrium domain
dwrate*	day^{-1}	(MET,COMP)	SLPEST	1st order degradation rate for dissolved pesticide fraction in the equilibrium domain
dks2	day^{-1}	(MET,COMP)	SLPEST	1st order degradation rate in the non-equilibrium domain
pcncx	µg/g	(MET,COMP)	SLPEST, MAIN	Temporary storage variable
feq	-	(MET,COMP)	SLPEST, ECHO, EROSN, INITL	soil fraction of equilibrium domain (Streck-Model)
f_neq	-	(MET)	READIN, ECHO, INITL	soil fraction of the non-equilbrium domain (PEARL-model)
s2old	µg/g	(MET,COMP)	SLPEST, INITL, OUTPST	concentration in the non-equilibrium domain of the previous day
dkflx_eq	g/cm^2	(MET,COMP)	SLPEST, MASBAL, OUTPST,OUTTSR	decay flux in the equilibrium domain of each soil compartment
dkflx_ne	g/cm^2	(MET,COMP)	SLPEST, MASBAL, OUTPST,OUTTSR	decay flux in the non-equilibrium domain of each soil compartment
sdkfq	g/cm^2	(MET,COMP)	SLPEST, MASBAL, OUTPST,OUTTSR	sum of the decay flux in the equilibrium domain
sdkfn	g/cm^2	(MET,COMP)	SLPEST, MASBAL, OUTPST,OUTTSR	sum of the decay flux in the non-equilibrium domain
dks2_rel	day^{-1}	(MET,TRA)	READIN, ECHO, TRANSFORM_NEQ	relative transformation rate in the non-equilibrium domain

MET: number of metabolites, COMP: number of soil compartments, TRA: number of transformation routes

*: set to ‘0’ because this process is simulated in the traditional code in PELMO

As already mentioned the new model for dealing with sorption kinetics was implemented in the subroutine SLPEST. This subroutine sets up the coefficient matrix for the solution of the soil pesticide transport equation. It then calls an equation solver for the tridiagonal matrix and sets up pesticide flux terms using the new concentrations. The distribution between equilibrium and non-equilibrium sites and (possibly) the degradation in the non-equilibrium domain was implemented separately and before the traditional pesticide fate processes are handled in SLPEST. Consequently, the variables *dsrate* and *dwrate* in the new module were set to "0" because these processes are covered in the traditional part of the subroutine.

4.3 Fundamental algorithms of the Streck approach

The new code was programmed considering the following differential equation system (Chen and Wagenet, 1997):

1. Differential Equations

The differential equations and initial conditions are

$$\frac{d}{dt}\left[\theta C + \rho\left(S_1 + S_2\right)\right] = -\mu_1 \theta C - \left(\mu_{S_1}\rho S_1 + \mu_{S_2}\rho S_2\right) \qquad \text{Equation 1}$$

$$\frac{dS_1}{dt} = fKd\,\frac{dC}{dt} \qquad \text{Equation 2}$$

$$\frac{dS_2}{dt} = \alpha\left[(1-f)K_d C - S_2\right] - \mu_{S_2} S_2 \qquad \text{Equation 3}$$

With the initial conditions

$$C(0) = C_0$$

$$S_1(0) = fK_d C_0$$

$$S_2(0) = S_0$$

C: Concentration in the dissolved phase; µg/L.

C_t: total Concentration in the soil; µg/L.

S_1 Concentration in the instantaneous (equilibrium) adsorbed phase, µg/g.

S_2: Concentration in the kinetic adsorbed phase, µg/g.

f Soil fraction of the instantaneous adsorbed phase, dimensionless.

K_d Partition coefficient when adsorption/desorption equilibrium achieved, mL/g.

a First-order desorption rate constant in the kinetic adsorbed phase, day-1;

μ_{S1}: Degradation rate constant on the equilibrium adsorption site, day^{-1}.

μ_{S2}: Degradation rate constant on the kinetics adsorption site, day^{-1}

μ_1 Degradation rate constant in the soil pore water or liquid phase, day^{-1}

θ : Soil moisture content, cm³/cm³.

ρ: Soil bulk density, g/cm³.

t: Time, day.

The analytical solutions for these equations are as follows:

Equation 4 a:

$$C = \frac{C_0}{(\lambda_1 - \lambda_2)} P_{1c} + P_{2c}$$

Equation 4 b

$$S_1 = fK_d C$$

Equation 4 c

$$s_2 = \frac{\alpha(1-f)K_d C_0}{(\lambda_1 - \lambda_2)} \ \mathrm{P}_{1\mathrm{s}} + \frac{S_0}{(\lambda_1 - \lambda_2)} \ \mathrm{P}_{2\mathrm{s}}$$

Equation 5

$$C_t = \left(\theta + \rho f K_d\right)C + \rho S_2$$

Equation 5 is for real concentration both in the adsorbed phase and in the soil pore water. The dummy parameters in Equations 4 to 5 are defined below.

Equation 6 a

$$P_{1c} = \left(\alpha + \mu_{S_2} + \lambda_1\right)\exp\left(\lambda_1 t\right) - \left(\alpha + \mu_{S_2} + \lambda_2\right)\exp\left(\lambda_2 t\right)$$

Equation 6 b

$$P_{2c} = \frac{\omega S_0}{\left(\lambda_1 - \lambda_2\right)}\left[\exp\left(\lambda_1 t\right) - \exp\left(\lambda_2 t\right)\right]$$

Equation 7 a

$$P_{1s} = \left[\exp\left(\lambda_1 t\right) - \exp\left(\lambda_2 t\right)\right]$$

Equation 7 b

$$P_{2s} = \left(\alpha + \mu_{S_2} + \lambda_1\right)\exp\left(\lambda_2 t\right) - \left(\alpha + \mu_{S_2} + \lambda_2\right)\exp\left(\lambda_1 t\right)$$

Equation 8

$$\lambda_1 = \frac{1}{2}\left(-b + \sqrt{b^2 - 4c}\right)$$

Equation 9

$$\lambda_2 = \frac{1}{2}\left(-b - \sqrt{b^2 - 4c}\right)$$

Equation 10

$$b = \gamma + \mu_{S_2} + \mu_e$$

Equation 11

$$c = \mu_e\left(\alpha + \mu_{S_2}\right) + \mu_{S_2}\left(\gamma - \alpha\right)$$

Equation 12

$$\mu_e = \frac{\mu_{\mathrm{I}} + \left(R_1 - 1\right)\mu_{S_1}}{R_1}$$

Equation 13

$$\omega = \frac{\alpha\rho}{R_1\theta}$$

Equation 14

$$\gamma = \frac{\alpha R}{R_1}$$

Equation 15

$$R_1 = 1 + \frac{f\rho K_d}{\theta}$$

Equation 16

$$R = 1 + \frac{\rho K_d}{\theta}$$

This analytical solution was implemented into PELMO in its subroutine SLPEST. The respective source code is listed in Appendix A.

As shown by the equations presented in this chapter the whole implementation of kinetic sorption is based on linear sorption. However, PELMO is calculating sorption in soil according to the non-linear Freundlich approach.

Both processes, kinetic sorption and equilibrium sorption according to Freundlich are linked in the new version of PELMO using a stepwise approach which recalculates the equilibrium in soil directly after the changes caused by the kinetic sorption have been calculated.

Of course, such a stepwise approach necessarily will produce little deviations compared to a simultaneous procedure but due to the small time step of not more than one day in PELMO the errors can be considered very small.

Last but not least, the results of the example simulations presented in chapter 5 demonstrate that the procedure works well

4.4 Relationship between Streck and PEARL parameters

As already mentioned other realisations of non-equilibrium sorption with slightly different parameter definitions but mathematically identical results have been developed.
PEARL describes non-equilibrium sorption using the following equation:

Equation 17

$$c^* = \theta \cdot c_L + \rho\left(S_{EQ,PEARL} + S_{NE,PEARL}\right)$$

Equation 18

$$S_{EQ,PEARL} = K_{F,EQ} \cdot c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^N$$

Equation 19

$$\frac{dS_{NE,PEARL}}{dt} = k_{d,PEARL}(K_{F,NE}c_{L,R}\left(\frac{c_L}{c_{L,R}}\right)^N - S_{nE,PEARL})$$

Equation 20

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

Equation 21

$$R_t = -k_t\left(\theta \cdot c_L + \rho S_{EQ,PEARL}\right)$$

c^* = total concentration (mg/L)

c_L = concentration in the liquid phase (mg/L)

$c_{L,R}$ = reference concentration in the liquid phase (mg/L)

θ = volume fraction of water (-)

$S_{EQ,PEARL}$ = content sorbed at equilibrium sites (mg/kg)

$S_{NE,PEARL}$ = content sorbed at non-equilibrium sites (mg/kg)

$K_{F,EQ}$ = equilibrium Freundlich sorption coefficient (L/kg)

$K_{F,NE}$ = non-equilibrium Freundlich sorption coefficient (L/kg)

N = Freundlich exponent (-)

$k_{d,PEARL}$ = desorption rate coefficient (d^{-1})

$f_{NE,PEARL}$ = factor for describing the ratio between the equilibrium and non-equilibrium Freundlich coefficients in PEARL(-)

R_t = rate of degradation in soil (mgL^{-1}d^{-1})

The main difference compared to the Streck model is the definition of f_{NE} which is the ratio of non-equilibrium sites to equilibrium sites here, not to the sum of both. This is also influencing the sorption constant $K_{f,eq}$.

The total Freundlich sorption coefficient $K_{F,tot}$ is defined in PEARL as follows

Equation 21

$$K_{f,tot} = K_{F,eq} + K_{F,neq} = \left(1 + f_{neq,PEARL}\right) * K_{F,eq}$$

However, the parameter both models are using can be easily transferred based on the following equations:

Equation 21

$$k_{d,PEARL} = \frac{\alpha_{STRECK}}{1 - f_{EQ,STRECK}}$$

Equation 21

$$k_{NE,PEARL} = \frac{1 - f_{EQ,STRECK}}{f_{EQ,STRECK}}$$

In the new shell around PELMO these transformation factors have been implemented and it is possible to use either the PEARL or the Streck parameters in the model (more information on how this can be done is given in the next chapter).

As explained earlier some extensions were made in the file “echo.plm” to report the current parameter setting with respect to kinetic sorption (see the example in Table A 2)

Table A 2: New version of „echo.plm“ reporting parameter setting used for the simulation

```
SORPTION PARAMETERS
-------------------


  --PARAMETERS TO CALCULATE KD-VALUES WITH KOC--
      KOC [CM**3/G]                                                 60.00
      FREUNDLICH-SORPTION EXPONENT 1/n                             0.9000
      MIN. CONC FOR FREUNDLICH-SORPTION [æG/L]                     0.1000E-01
      INCREASE OF SORPTION PER YEAR [%]:                           0.0000

      EQUILIBRIUM CONSTANT FOR DOC[L/kg]:                          0.0000
      DOC IN SOIL WATER [MG/L]:                                    0.0000
      ESTIMATED MOISTURE FOR AIR DRIED SOIL(m3/m3):                0.7200E-02
      RESULTING REL. CHANGE OF SORPTION COEFF. (-):                0.0000
      [PEARL] FACTOR DESCRIBING NON-EQ-SITES EQ-SITES (-):         0.3000
      [PEARL] DESORPTION RATE [1/D]:                               0.1000E-01
```

For summarising the results of the simulation modifications have been made in the subroutine “outpst” which writes output into the file “chem.plm”. A new column was added at the right hand side of the table where the fluxes and storages for a certain period (day, month, year) are reported (“storage in neq domain”). An example is shown in Table A 3.

Table A 3: New version of „chem.plm“ reporting storage in kinetic sorption domain

```
FLUXES AND STORAGES FOR THIS PERIOD
 -----------------------------------
FOLIAR         PREVIOUS                         FOLIAR                            FOLIAR            CURRENT
APPLICATION    STORAGE           DECAY          VOLATILISATION WASHOFF            PENETRATION       STORAGE

0.000        0.0000            0.0000         0.0000            0.0000            0.0000         0.0000
CANOPY

HO-COM- SOIL     PREVIOUS   LEACHING     DECAY*     GAS**    PLANT     LEACHING    CURRENT      STORAGE IN
     APPLICATION  STORAGE    INPUT              DIFFUSION   UPTAKE    OUTPUT      STORAGE      NEQ-DOMAIN
  -------------------------------------------------------------------------------------------------------


1  1    0.2000E-01 0.0000     0.0000    0.5662E-03  0.0000    0.0000      0.0000   0.1943E-01    0.3097E-02
1  2    0.4800     0.0000     0.0000    0.1359E-01  0.0000    0.0000      0.0000   0.4664        0.7433E-01
1  3    0.5000     0.0000     0.0000    0.1415E-01  0.0000    0.0000      0.0000   0.4858        0.7743E-01
```

5 Results of example simulations

In order to test the new implementation several test simulations were performed with PELMO and compared with respective results of PEARL. However, PELMO and PEARL are rather different with respect to the simulation of soil hydrology. In order to check the kinetic sorption routines in both models without interfering effects due to differences in soil moisture calculations further processes in the models were switched off as much as possible. The endpoint for the comparison was the time dependent soil concentration in the top 5 cm. A summary about the simulation conditions is given in Table A 4.

Table A 4: Parameter selection for the example simulations

Parameter/Process	Test 1	Test 2	Test 3	Test 4	Test 5***	Test 5***
Molecular mass (g/mol)	300	300	300	300	300	300
KOC (L/kg)	60	60	1000	60	60	60
Freundlich exponent (-)	0.9	0.9	0.9	0.9	0.9	0.9
PEARL f_{ne}	0.5	0.3**	0.3**	0.5	0.5	0.5
Streck f_{eq}	0.6666	0.7692	0.7692	0.6666	0.6666	0.6666
PEARL: k_{des} (day^{-1})	0.0	0.01**	0.01**	0.5	0.5	0.5
Streck: α (day^{-1})	0.0	2.307 10^{-03}	2.307 10^{-03}	0.1667	0.1667	0.1667
DEGT50 (d)	20	20	100	20	60	20
Relative degradation in kinetic sorption domain	0	0	0	0	0	0.5
Temperature correction	-	-	-	-	-	-
Application rate (kg/ha	1	1	1	1	-	1
Application date	01 Jan	01 Jan	01 Jan	01 Jan		01 Jan
Application depth (cm)	0-5	0-5	0-5	0-5		0-5
Soil	Borstel	Borstel	Borstel	Borstel	Borstel	Borstel
organic carbon in top soil (%)	1.5	1.5	1.5	1.5	1.5	1.5
Weather	artificial*	artificial	artificial	artificial	artificial	artificial

* no rainfall, potential evapotranspiration set to ‘0’, constant temperature of 20 °C

** recommended default setting for the kinetic sorption process

*** metabolite simulation based on test 2 simulation (formation fraction: 100 %)

5.1 *Example simulation 1*

The first simulation was performed to demonstrate that PEARL and PELMO calculate the same concentrations in soil if the new kinetic sorption routine in PELMO has been switched off by setting PEARL k_{des} (or Streck α) to zero.

The result of the comparison is shown in Figure A 2

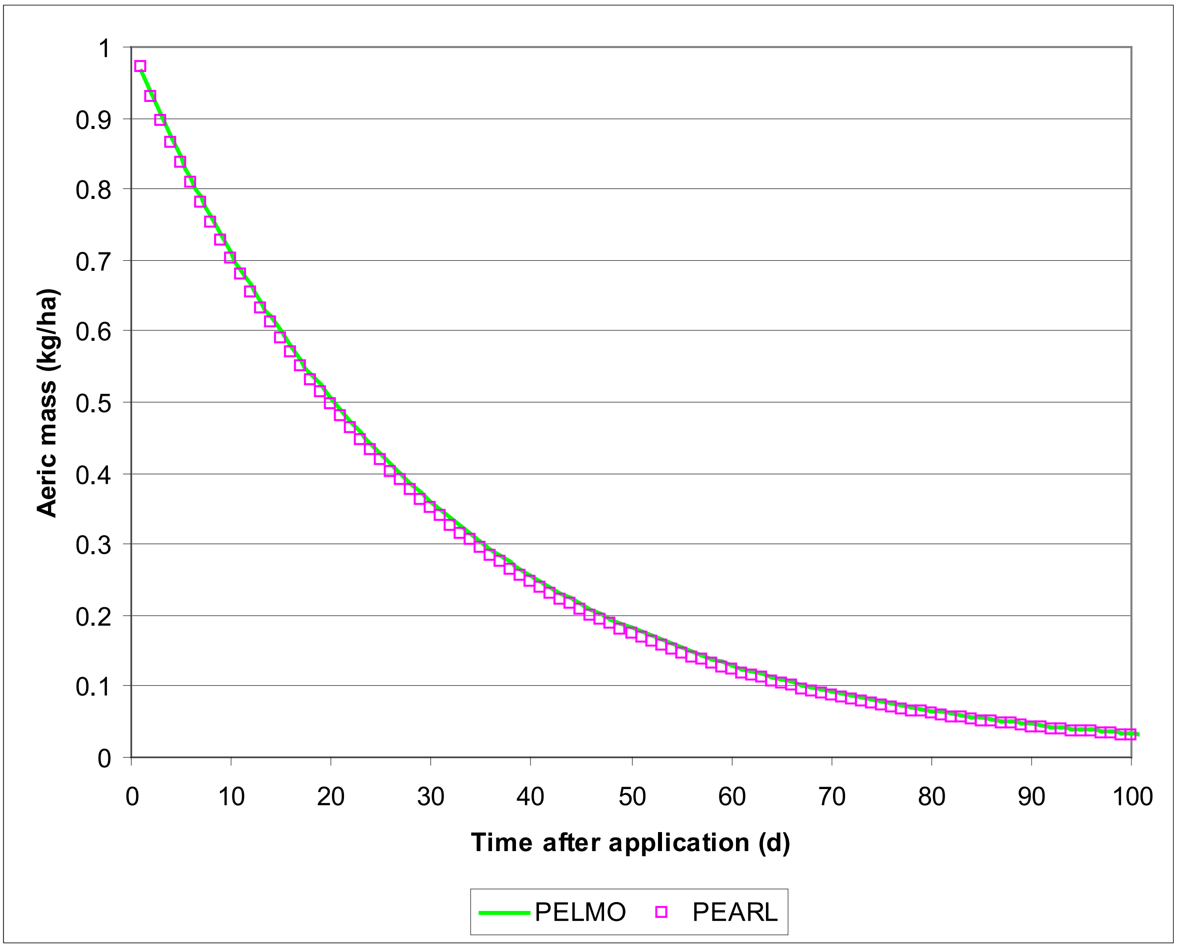

Figure A 2: Calculated time dependent areic masses in top 5 cm soil (Example 1)

As expected there are no differences between the PELMO and PEARL simulations. The main difference between the computer models, the different calculation of soil hydrology, is irrelevant because in the simulation rainfall and evapotranspiration have been switched off.

5.2 Example simulation 2

In the second simulation the new kinetic sorption process was considered in both models. The default parameter setting according to FOCUS (2009) was used for the simulation:

- PEARL k_{des} = 0.01 day^{-1} (equivalent to Streck $\alpha = 2.307\ 10^{-03}$ day^{-1}) and
- PEARL f_{neq} = 0.3 (equivalent to Streck f_{eq} = 0.7692).

The result of the comparison is shown in Figure A 3.

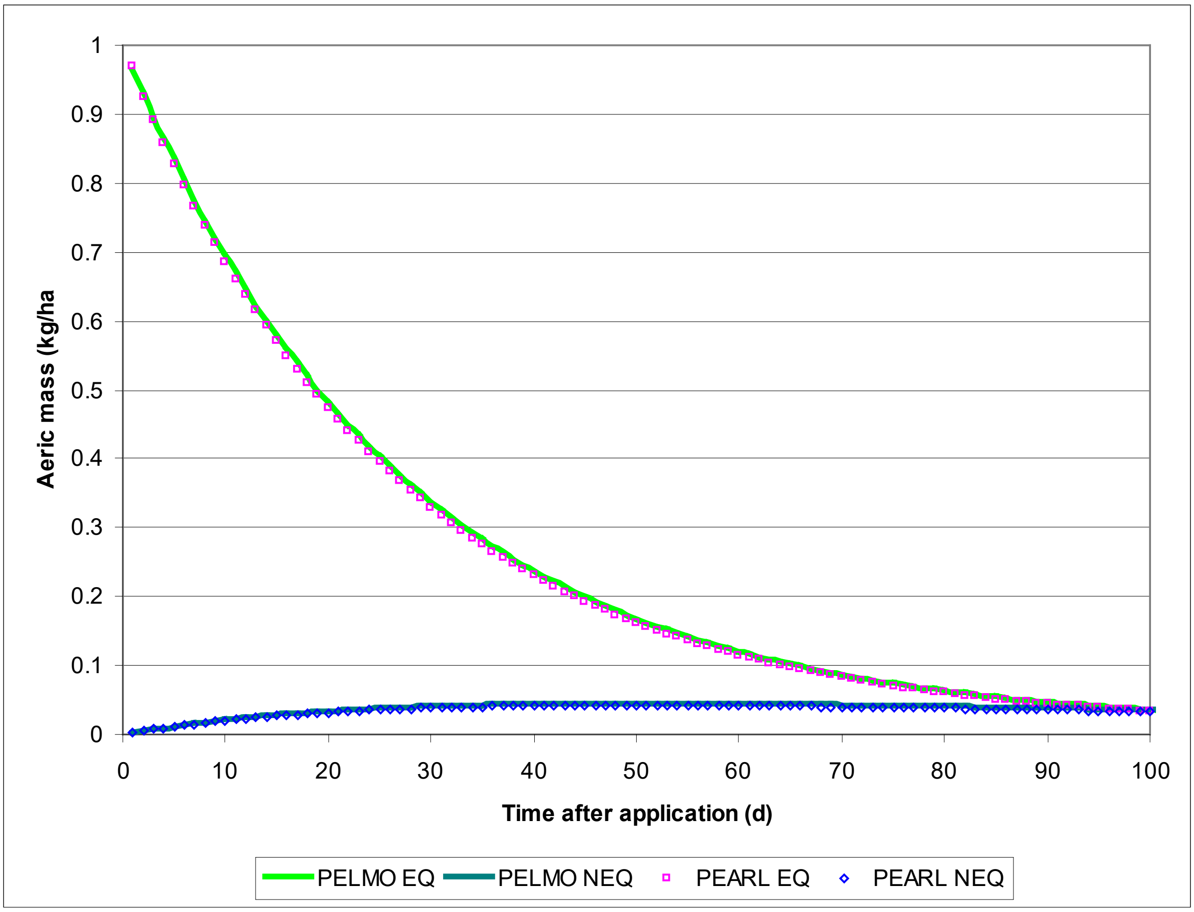

Figure A 3: Calculated time dependent areic masses in top 5 cm soil (Example 2)

The calculated mass content in the top 5 cm of the two models match perfectly for the equilibrium domain (EQ) as well as for the non-equilibrium (NEQ) kinetic sorption domain. Obviously, both approaches (Streck and PEARL method) lead to the same distribution in soil and the new process in PELMO was implemented satisfactory.

5.3 *Example simulation 3*

In the next simulation the same kinetic sorption parameters has been used as in the previous example

- PEARL k_{des} = 0.01 day^{-1} (equivalent to Streck $\alpha = 2.307\ 10^{-03}\ day^{-1}$) and
- PEARL f_{neq} = 0.3 (equivalent to Streck f_{eq} = 0.7692).

but with different sorption and degradation parameter setting. Whereas in the previous example pesticide D (FOCUS 2000) was considered for the test a more persistent and stronger sorbing compound was simulated:

- KOC = 1000 L/kg and
- DEGT50 = 100 d.

The result of this comparison is shown in Figure A 4.

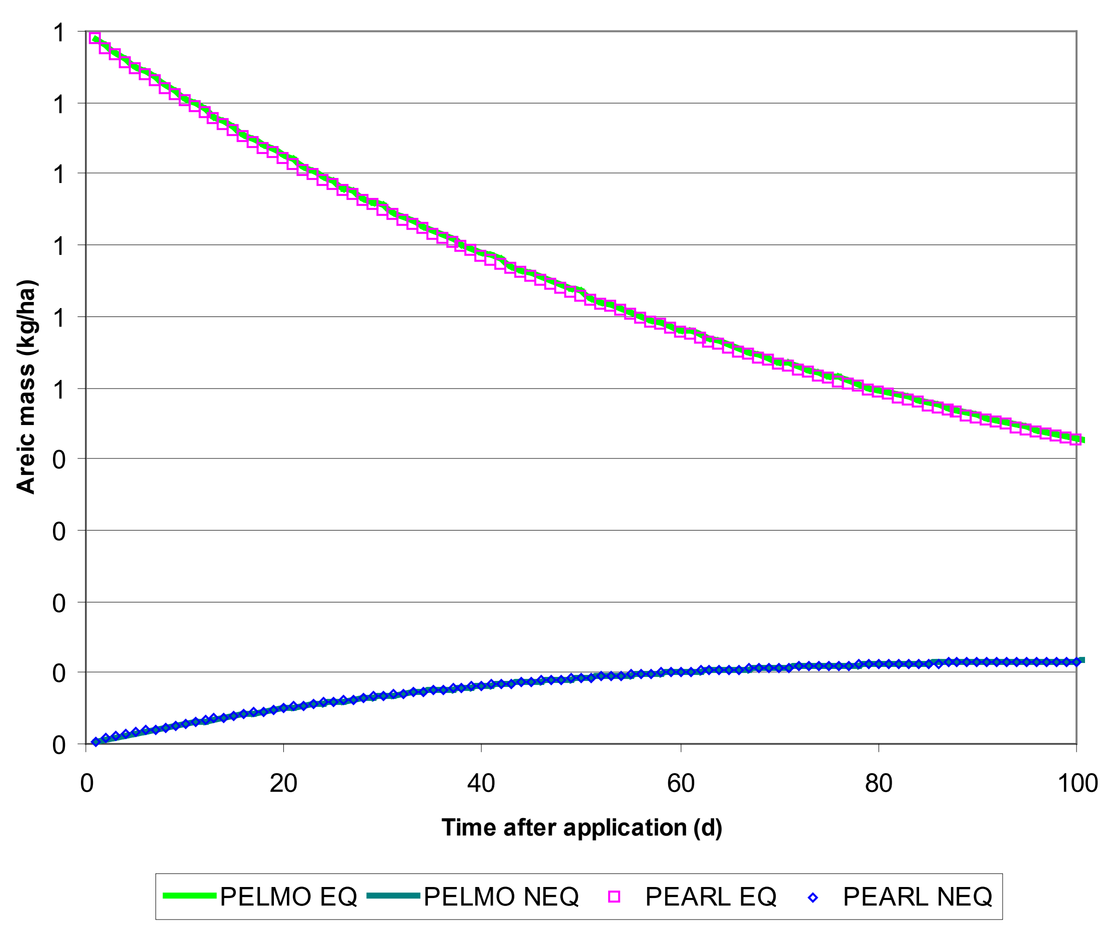

Figure A 4: Calculated time dependent areic masses in top 5 cm soil (Example 3)

Also in this test simulation the results of PEARL and PELMO perfectly match, the dynamic content in the equilibrium domain as well as the non-equilibrium domain. Obviously, both weak and strong sorbing compounds are simulated adequately by the new kinetic sorption model in PELMO.

5.4 Example simulation 4

In the fourth test simulation pesticide D (FOCUS 2000) has been combined with extreme kinetic sorption parameters to check whether both models also gives good correlation in this exceptional case

- PEARL k_{des} = 0.5 day^{-1} (equivalent to Streck $\alpha = 0.1667$ day^{-1}) and
- PEARL f_{neq} = 0.5 (equivalent to Streck f_{eq} = 0.6667).

The result of this comparison is shown in Figure A 5.

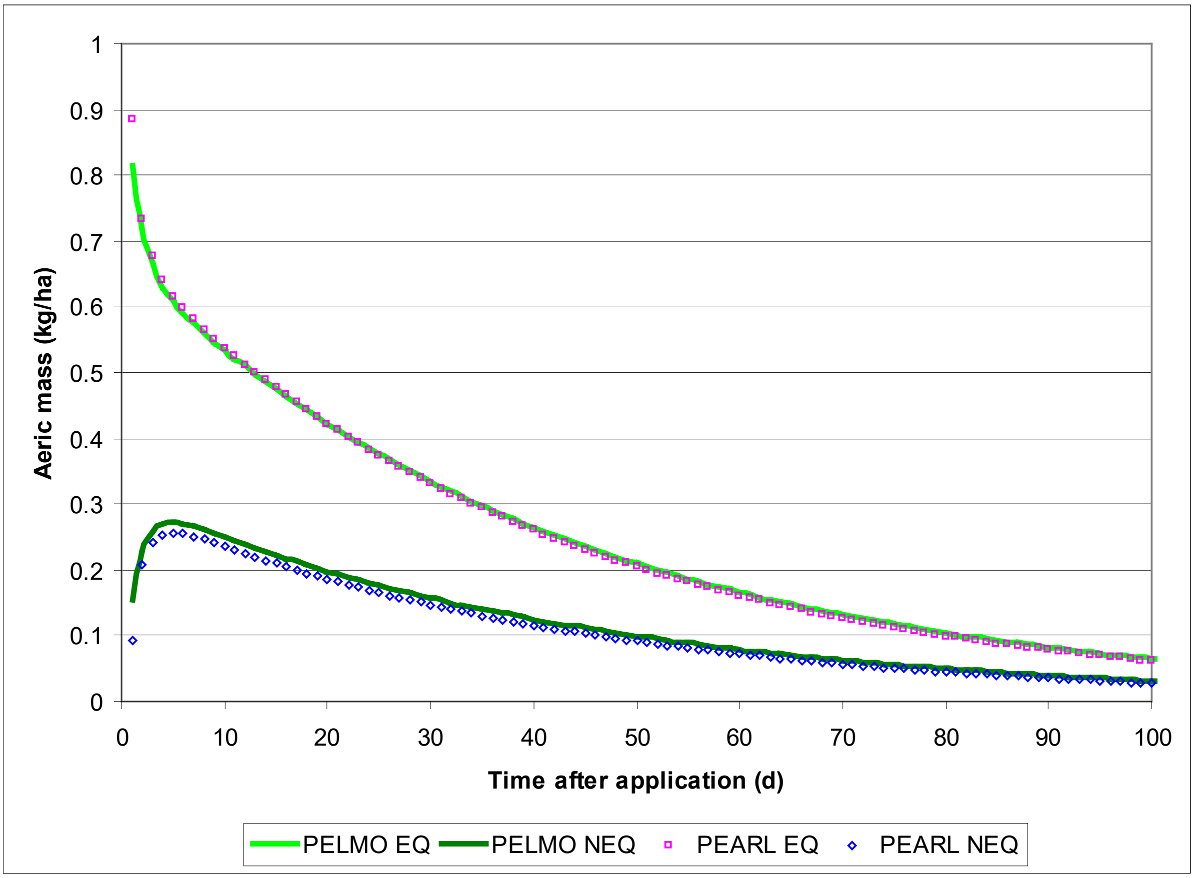

Figure A 5: Calculated time dependent areic masses in top 5 cm soil (Example 4)

In this extreme test simulation minor differences between PEARL and PELMO can be noticed for the pesticide content in the non-equilibrium domain. However, the differences are rather small and the shape of the curves is nevertheless very similar. Moreover, simulated content in the equilibrium domain matches perfectly.

5.5 Example simulation 5

In the final simulation the fate of a test substance is simulated formed by test substance 2 was analysed. For the metabolite the same extreme kinetic sorption parameters has been selected as in the previous run

- PEARL k_{des} = 0.5 day^{-1} (equivalent to Streck $\alpha = 0.1667$ day^{-1}) and
- PEARL f_{neq} = 0.5 (equivalent to Streck f_{eq} = 0.6667).

The result of this comparison is shown in Figure A 6.

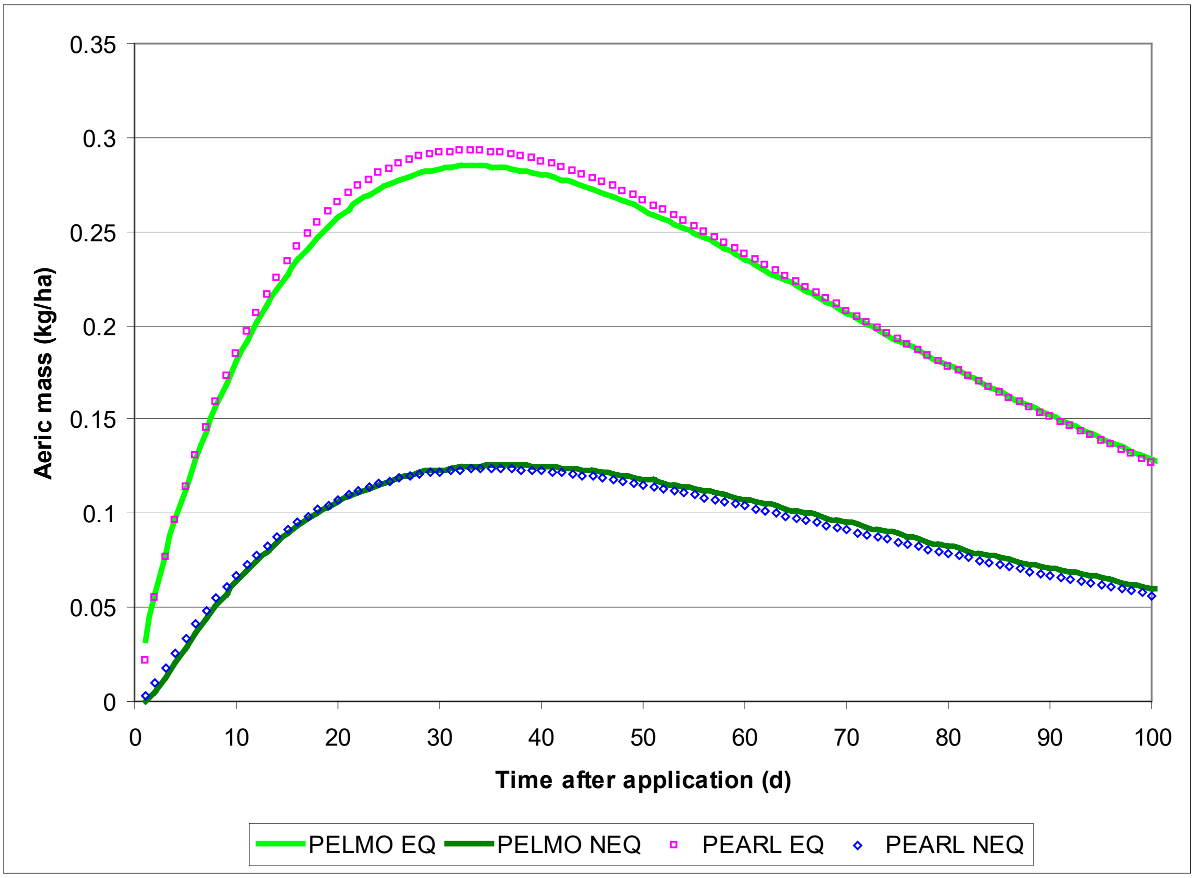

Figure A 6: Calculated time dependent areic masses in top 5 cm soil (Example 5)

Also the results of test simulation 5 show good agreement between PEARL and PELMO under extreme parameter settings.

5.6 *Example simulation 6*

In this simulation a compound is simulated having the same properties as test substance 4 but with additional degradation in kinetic sorption domain (relative degradation factor: 0.5).

The result of this comparison is shown in Figure A 7. In this example a comparison is made between two PELMO simulations (test 2 and test 6) because PEARL is not able to consider degradation at non-equilibrium sites.

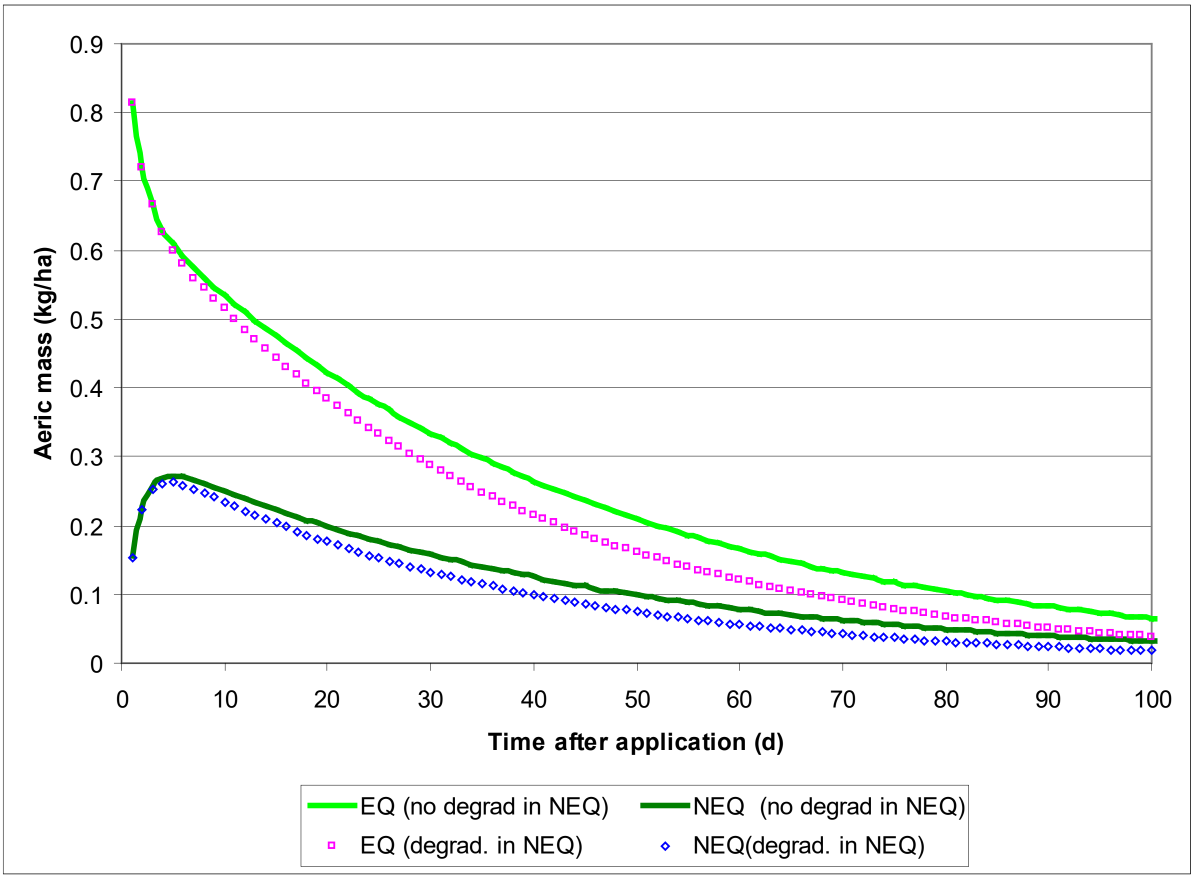

Figure A 7: Calculated time dependent areic masses in top 5 cm soil (Example 6)

The figure shows the expected effect on the time dependent soil concentrations: if degradation is considered at non-equilibrium sites the concentration decline is faster than without assuming this additional degradation process. Due to non-linear dependencies the process may have a significant effect on possible concentrations in the percolate even if the difference in the top soil is relatively small.

5.7 *Example simulation 7*

In the final simulation series three variations of (FOCUS) Pesticide D is simulated with annual applications in winter cereals (1 kg/ha one day before crop emergence).
Following variations were considered with respect to kinetic sorption:

- Without kinetic sorption
- Default kinetic sorption (PEARL: f_{ne} = 0.3, k_{des}: 0.01 1/d
- Extreme kinetic sorption (PEARL: f_{ne} = 0.5, k_{des}: 0.5 1/d

The result of this comparison is shown in Table A 5 and Figure A 8. Dependent on the location different simulation periods have been found for calculating the 80th percentile dependent on the kinetic sorption parameters.

Table A 5: Annual concentrations in the percolate (80th percentile) for FOCUS D (annual applications in winter cereals

Variation	No kinetic sorption				Default kinetic sorption				Extreme kinetic sorption			
DEGT50adjusted*	20 d				16 d				14 d			
Location	Perc.	Pest flux (g/ha)	Percolate (L/m²)	C (µg/L)	Perc.	Pest flux (g/ha)	Percolate (L/m²)	C (µg/L)	Perc.	Pest flux (g/ha)	Percolate (L/m²)	C (µg/L)
Châteaudun	(9/11)	0.06466	212.74	0.03	(9/11)	0.013414	212.74	0.006	(9/11)	0.003004	212.74	0.001
Hamburg	(7/8)	10.835	576.1	1.869	(10/8)	3.295	463.4	0.703	(8/10)	1.34	463.4	0.295
Jokioinen	(5/10)	2.2524	533.2	0.423	(10/9)	1.0364	735.6	0.143	(9/13)	0.160728	442.04	0.036
Kremsmünster	(3/13)	4.954	912	0.541	(9/3)	1.1696	682.1	0.173	(9/14)	0.18958	411.1	0.046
Okehampton	(6/1)	17.187	953.9	1.804	(6/1)	6.458	953.9	0.678	(1/20)	3.679	997.5	0.369
Piacenza	(5/11)	6.888	662.8	1.028	(11/5)	2.923	662.8	0.442	(5/12)	1.6076	639.9	0.247
Porto	(12/11)	32.51	1254.5	2.601	(12/6)	12.091	926	1.236	(4/11)	11.497	1513.1	0.723
Sevilla	(3/15)	0.07078	571.1	0.014	(3/15)	0.03768	571.1	0.007	(3/15)	0.006695	571.1	0.001
Thiva	(12/6)	0.09342	232.1	0.04	(6/12)	0.03087	232.1	0.013	(12/6)	0.006465	232.1	0.003

* assuming linear sorption and a k_d of 1 L/kg in the soil independent on the location

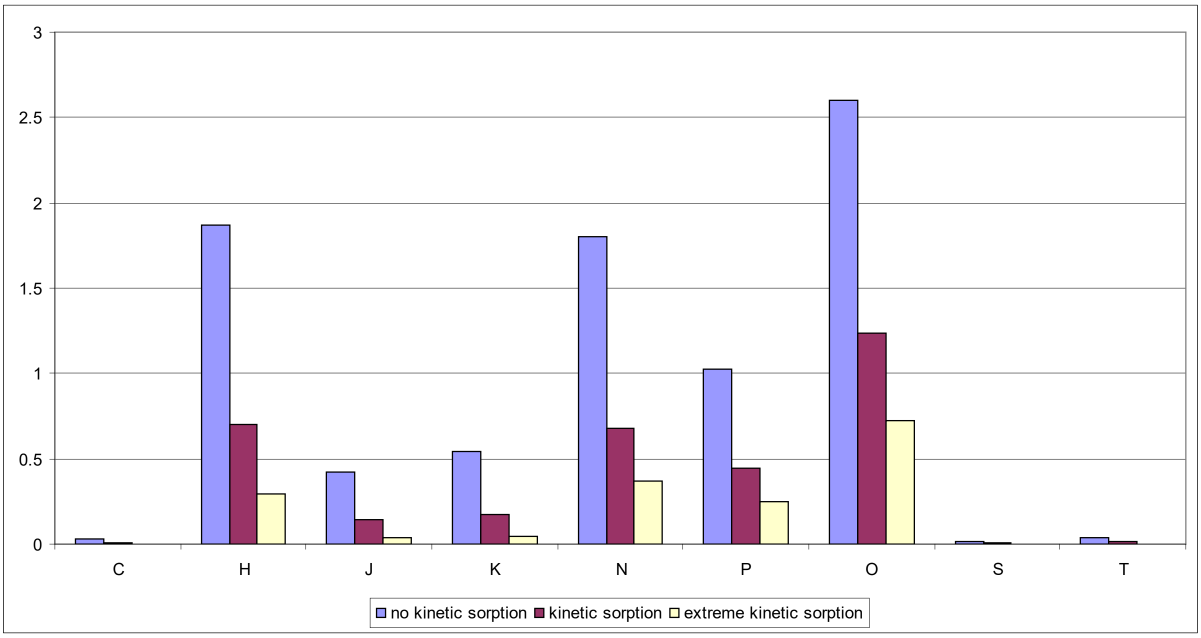

Figure A 8: Effect of kinetic sorption at various FOCUS location (80th percentile)

As shown in Figure A 8 there is a clear dependency of kinetic sorption on the annual concentrations. The concentrations are decreasing if kinetic sorption is considered because the residence time in a certain soil layer will increase which gives more time degradation.

6 Modifications in input data files

If the user wants to consider kinetic-sorption for a simulation and enters the necessary parameters in the shell the values are written into PELMO's psm-file.

Therefore, the format of the sorption and degradation section in this input file had to be modified. Relative degradation in the non-equilibrium domain is written in the last numerical column of the degradation table as shown in Table A 6. Different relative degradation constants can be considered for all degradation routes for a certain compound. The same format was chosen for parent compounds and metabolites

Table A 6: Extended degradation section in PELMO's psm file to consider relative degradation

```
<DEGRADATION>
<deg rate  deg temp     q10      moist-abs   moist-rel   moist-exp   rel deg neq sites
 0          0           0           0           0           0            0        <Met A1>
 0          20          2           19          0           0            0        <Met B1>
 0          20          2           19          0           0            0        <Met C1>
 0          20          2           19          0           0            0        <Met D1>
 0.034657   20          2.2         0           100         0.7          0        <BR/CO2>
```

For including the other kinetic sorption related parameters the sorption section was extended.

Table A 7: Extended sorption section in PELMO's psm file to consider kinetic sorption

```
<ADSORPTION>
<Koc-value  Fr.exp.Koc  pH pKa  limit for Freundl.  ann.incr.> <k_doc> <% change> KOC2 pH2 f_neq   kdes>
   60        0.9      -99   20        0                0          0          0   -99    -99   0.3    0.01
<END ADSORPTION>
```

The columns in Table A 7 have the following meaning:

Koc-value:	KOC-value of the compound (L/kg)
Fr.exp.Koc:	Freundlich exponent of the KOC-value
pH:	pH-value at which the sorption study was performed[2]
pKa:	pKa-value of the compound[2]
limit for Freundl.sorption:	conc. at which the Freundlich sorption switches to linear-sorption
ann.incr:	annual decrease of sorption constant (linearly, %)
k_doc	complexation constant to Doc (-)[1]
% change	relative increase of sorption of soil is air dried (-)[3]
KOC2	KOC-value of the compound at pH2[2]
pH2	pH2-value at which the sorption study was performed[2]
f_neq	soil fraction of the non-equilibrium domain (PEARL-model)
kdes>	1st order desorption rate at non-equilibrium sites (PEARL-model)

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[1] only relevant if Doc content in soil is > 0

[2] only relevant if sorption in soil is dependent on pH

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