Ch. 8 Pesticide fate

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8.1 Introduction

The pesticide balance model is a specialization of the general solute balance model. Thus, it includes the transport and sorption processes for solutes (see Chapter 6), and additionally decomposition and generation of metabolites can be simulated. Input of pesticides to the system is typically simulated with a spraying action (dry amounts), or alternatively with irrigation (see Chapter 10). The pesticide then moves through the surface compartments (see Chapter 3), before it infiltrates the soil. When accounting for pesticide fate in the plant-soil-water-system, only the active ingredient of the pesticide is simulated. Additionally, formation and fate of metabolites can be simulated, if relevant.

The pesticide balance model can also be used to simulate the fate of plant toxins. These are generated in the above-ground-biomass and released from the plants (see appendix 3.X)[1], before they infiltrate the soil.

Pesticide processes can be described using the standard functions (submodule *default*) or by using the submodule *FOCUS*, which includes a parameterisation of the pesticides as close as possible to the FOCUS parameterization (FOCUS, 2012). These are described in section 8.2.1 and 8.2.2, respectively.

For a general discussion on relevant processes and processes descriptions when simulating the fate of pesticide in the agro-eco-system is referred to the original final reports from the FOrum for the Coordination of pesticide models and their Use (FOCUS) on leaching to surface water (Adriaanse et al., 1997), leaching to groundwater (Boesten et al., 1995) and persistence in the soil (Boesten et al., 1997), which can be found her.

8.2 Definition of a pesticide

To function as a solute in Daisy, the pesticide must be defined. Some examples are available under "lib" in the Daisy directory (see *chemistry-base.dai* and *chemistry.dai*), halflifes and adsorption parameters for these are seen on Figure 8.1. Other pesticides (and plant toxins) can be specified by the user. Additionally, the pesticide parameterizations can be used to build other types of chemicals and evaluate their fate in the plant-soil-water-system.

The pesticides are defined in a hierarchical system, where the sub-groups inherit the parameter definitions from the "parent"-definition. Three "parent" definitions exist: *FOCUS, Default,* and *Nutrient,* these all share the chemical *base* parameters (see Chapter 6).

Nutrient is described in chapter 7.

Default has two predefined chemicals: *classic* which can be used to represent a chemical where no specific information is available and *solid* that represents non-dissolvable chemicals.

[1] Appendix 3.X is not yet available. There is referred to (García-Jorgensen et al., 2020)

FOCUS contains all the predefined pesticides and the predefined metabolite. Their parameterization is inspired by the *Generic guidance for FOCUS surface water Scenarios* (FOCUS, 2012). Thus, the parameterization of above ground processes (*canopy_dissipation_halftime* 240 [h] and *canopy_washoff_coefficient* 0.075 [h] (see Chapter 3 and appendix 3.3)), the *diffusion_coefficient* ($5e^{-6}$ [$cm^2\ s^{-1}$] (see Chapter 6) and the decomposition modifier function for temperature, water and depth (see 8.3.2) follows FOCUS, 2012.

User specified new pesticides and plant toxins can be parameterized based on any of the existing parameterizations and will then inherit the parameters of the "parent"-chemical.

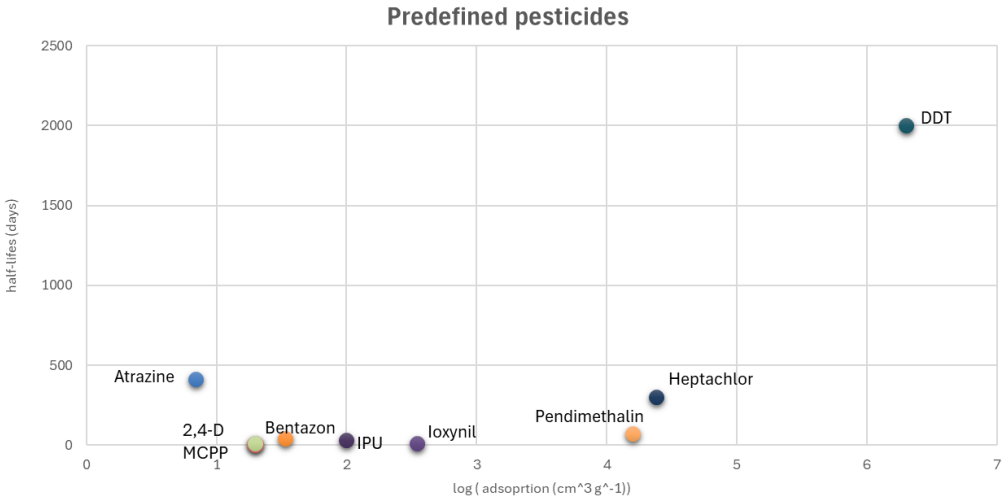

Figure 8.1: Half-life and adsorption of predefined pesticides in Daisy

The predefined pesticides are of older date and we recommend to check the Pesticide Properties Database (PPDB - Pesticides Properties DataBase) for updated adsorption and degradation values.

8.3 Decomposition

Decomposition of pesticides in the soil is described by first order kinetics as:

$$\xi = -[K^* f_T(T) f_h(h) f_z(z) f_{CO_2}(\xi_{CO_2}) f_C(C) f_\tau(\tau) f_{SMB}(SMB)] \cdot C_s \qquad (8.1)$$

where

ξ = the decomposition rate [g h^{-1}]

K^* = the decomposition rate coefficient [h^{-1}]

C_s = the chemical content in the soil [g cm^{-3}]. Thus, decomposition is calculated for the total chemical content both sorbed and in solution, and

$f_T, f_h, f_{CO_2}, f_C, f_z, f_\tau$ and f_{SMB} = modifier functions (plf's) responding to the effect of temperature, T [C°], soil water pressure potential, h [cm], carbon dioxide evolution, ξ_{CO_2} [CO_2 h^{-1}], solute concentration, C [g cm^{-3}], depth, z [cm], lag time, τ [-], and size of the soil microbial pool, SMB [g C cm^{-3}] , respectively.

The decomposition rate coefficient

The decomposition rate coefficient must be parameterized with either *decompose_rate* [h^{-1}] or *decompose_halftime* [h^{-1}]. The *decompose_rate* = *ln(2)/decompose_halftime* so only one of the two should be specified.

The modifier functions for solute concentration, $f_C(C)$, and the modifier function for lag time, $f_\tau(\tau)$, are shared by all chemicals (defined in the *base* model). The modifier functions for temperature, moisture and depth are specific for the *default* description and the *FOCUS* description (part 8.3.1 and 8.3.1, respectively). The modifier function for CO_2 and SMB is only implemented for the default description (part 8.3.1).

Concentration effect

The modifier function f_C accounts for the influence of concentration level on the decomposition. The default value is 1, e.g. there is no effect of the pesticide concentration level on decomposition. However, it is possible to specify an effect using the *decompose_conc_factor* which takes a pairwise-linear-function of concentrations [g cm^{-3} H_2O] and effects [-].

Lag time effect

The modifier function f_τ accounts for possible lag time between allocation of a pesticide and beginning of decomposition. By default, there is no lag on decomposition. The lag modifier function assumes either the value 0 (no decomposition) or the value 1 (decomposition).

The lag modifier function is parameterized with the *decompose_lag_increment* parameter which takes a pairwise-linear-function of concentrations [g cm^{-3}] and lag increments [h^{-1}].

When the simulation starts, all nodes in the soil column has a lag value of 0. For each time step the optional state variable *lag* is increased with the value corresponding to the current concentration in each node. When *lag* in at least one node reaches 1.0 decomposition in the entire soil column begins. The state variable *lag* will continue to be 1 independent of the concentration.

Decomposition in two domains

When simulating solute transport in two domains (primary and secondary) the decomposition is calculated for the two domains separately with the same decompose rate coefficient and modifier functions. However, if a concentration effect, f_C, is included the effect will be calculated separately for the primary and secondary domain based on the concentration of chemical in each domain and the decomposition rate for the two domains will then differ.

Decomposition of chemicals in biopores is neglected.

Decomposition at the soil surface

As default, the decomposition processes at the soil surface are described with surface dissipation. However, if it is assumed that the decomposition processes in the soil dominates the breakdown processes at the soil surface, the decomposition factors for the soil can be used at the soil surface by activating *soil_affects_surface_decompose.* Similarly, if it is assumed that the breakdown processes at the surface generate metabolites, the *enable_surface_products* should be activated. By default, both *soil_affects_surface_decompose* and *enable_surface_products* are FALSE.

8.3.1 The default option

The modifier functions for temperature, moisture, depth, CO_2 and SMB in the *default* option is described below.

Temperature effect

The modifier function f_T accounts for the effect of temperature on the decomposition. The default assumption is that pesticide decay can be treated like other forms of carbon turnover with regards to the effect of temperature. Thus, for default chemicals, the temperature effect on decay will follow that for carbon (see Chapter 9), if not otherwise specified. Alternatively, a user specified effect can be applied using the parameter *decompose_heat_factor* which takes a pairwise-linear-function of degrees [C°] and effects [-]. Linear interpolation will be applied between the given points. The temperature modifier function is scaled so it is one at reference temperature (T_{ref} = 10 C°).

Moisture effect

The modifier function $f_h(h)$ accounts for the effect of moisture on the decomposition. The default assumption is that pesticide decay can be treated like other forms of carbon turnover with regards to the effect of moisture. Thus, for default chemicals, the moisture effect on decay will follow that for carbon (see Chapter 9), if not otherwise specified. Alternatively, a user specified effect can be applied using the parameter *decompose_water_factor* which takes a pairwise-linear-function of water [cm] and effects [-]. Linear interpolation will be applied between the given points.

Depth effect

The modifier function $f_z(z)$ accounts for the effect of depth on the decomposition. The default value is 1, e.g. there is no effect of depth on the decomposition. However, it is possible to specify an effect using *decompose_depth_factor* which takes a pairwise-linear-function of depths [cm] and effects [-]. Linear interpolation will be applied between the given points.

CO_2 effect

The modifier function f_{CO_2} accounts for the influence of CO_2 concentration level on the decomposition. The default value is 1, e.g. there is no effect of the CO_2 concentration level on the decomposition. However, it is possible to specify an effect using the *decompose_CO2_factor* which takes a pairwise-linear-function of concentrations rates [g CO_2-C cm^{-3} h^{-1}] and effects [-]. Linear interpolation will be applied between the given points. Depending on the CO_2-C content of the soil simulated as $C0_2$ production by the soil organic matter model (see Chapter 9), the corresponding effect is applied in the calculation of the decomposition rate (Eq. 8.1).

SMB effect

The modifier function f_{SMB} accounts for the influence of the amount of microbial-C on decomposition. It is by default 1 as KM = 0, e.g. there is no effect of the SMB-C content on the decomposition. The modifier function is calculated as (Vuaille et al., 2024):

$$f_{SMB} = \frac{SMB_C}{KM + SMB_C} \tag{8.2}$$

where

KM = the Michealis-Menten kinetics parameter [g C cm^{-3}] (default 0) and,

SMB_C = the carbon content in the specified SMB pool [g C cm^{-3}] (default 1, which corresponds to SMB2, 0 corresponds to SMB1 and -1 to all SMB pools).

The SMB modifier function is scaled so it is one at reference SMB-C content (SMB_ref [g C cm^{-3}]). By default, the SMB modifier function will not be scaled.

8.3.2 The FOCUS option

The modifier functions for temperature, moisture and depth in the $FOCUS$ option is described below.

Temperature effect

The modifier function f_T accounts for the effect of temperature on the decomposition. The temperature effect following the FOCUS recommendation (FOCUS, 2012) is given by:

$$F^T(T) = \begin{cases} 0.0 & 0 \leq T \\ 0.2T \cdot e^{(\alpha(5-T_{ref})} & 0 < T < 5 \\ e^{(\alpha(T-T_{ref})} & 5 < T \end{cases} \quad (8.3)$$

where

α = temperature effect parameter, by default 0.0946 [K^{-1}] and

T_{ref} = 20 dg [C°]

A comparison between the default temperature effect and the FOCUS temperature effect can be seen in appendix 3.3.

The temperature modifier function is scaled so it is one at reference temperature (T_{ref} =20 C°).

Moisture effect

The modifier function f_w accounts for the effect of moisture on the decomposition. The moisture effect following the FOCUS recommendation (FOCUS, 2012) is a function of both the pressure potential and water content calculated as:

$$F^w(w) = \begin{cases} 1 & pF \leq h \\ \left(\dfrac{\theta - 0.5\theta_{wp}}{\theta_{fc} - \theta_{wp}}\right)^B & 0 < T < 5 \\ 0 & 0.5\theta_{wp} > \theta \end{cases} \quad (8.4)$$

where

θ_{wp} and θ_{fc} = the water content [cm^3 cm^{-3}] at field capacity and wilting point respectively, and

B = soil moisture effect parameter, by default 0.49 []

A comparison between the default moisture effect and the FOCUS moisture effect can be seen in appendix 3.3.

Depth effect

The modifier function f_z accounts for the effect of depth on the decomposition. The FOCUS option allocates one value (the z_factor) to each defined soil interval:

$$F^z(z) = \begin{cases} 1 & 30 > z \\ 0.5 & 30 < z < 60 \\ 0.3 & 60 < z < 100 \\ 0 & 100 < z \end{cases} \quad (8.5)$$

8.4 Metabolites

For the active ingredients of a pesticide (parents) degrading to metabolites (daughter products) the amount of formed metabolite can be calculated as a fraction based on the molecular weight of the decomposed primary solute. This requires that both the parent chemical and the metabolite is parameterized with the *molar_mass*. Subsequently, the fate of the metabolite will be simulated as if it was a pesticide with the advection-dispersion equation, potential sorption and degradation.

The amount of created metabolite is calculated based on the amount of decomposed parent chemical and a formation factor.

$$\Gamma_{met}^S = \Gamma_D^S * f_{met} \quad (8.6)$$

where

Γ_D^S = amount of decomposed parent chemical [g cm^{-3}] and

f_{met} = the formation factor []

If the molar mass is specified both for the parent chemical and the metabolite the formation factor will be mole based ($f_{met} = fraction \cdot \frac{daughter\ molar\ mass}{parent\ molar\ mass}$), otherwise it will be mass based ($f_{met} = fraction$). The *fraction* and daughter chemical (*chemical*) are parameterized under *decompose_products* of the parent chemical. The daughter chemical must be defined as a chemical on its own.

Γ_{met}^S is then added as a source term for the advection-dispersion equation (see chapter 6) of the metabolite.

If the solute transport is simulated with two domains (see chapter 6), Γ_D^S is calculated as a fraction of the decomposed parent chemical for the primary and secondary domain, respectively and added as a source sink to the primary and secondary domains of the metabolite.

8.5 Parameter overview

Table 8.1. Related Parameter names in Daisy.

Name and explanation		Model (in Daisy)	Parameter name (Daisy reference manual)	Default	Default unit
	Defines how fast the chemical dissipates on the canopy. Must be specified with either *canopy_dissipation_halftime* or *canopy_dissipation_rate* (see Chapter 3)	Focus	*canopy_dissipation_halftime*	240	[h]
	Fraction of the chemical that follows the water off the canopy (see Chapter 3)	Focus	*canopy_washoff_coefficient*	0.075	[h]
D_0	The diffusion coefficient (see Chapter 6)	Focus	*Diffusion_coefficient*	$5e^{-6}$	[$cm^2\ s^{-1}$]
K^*	The decomposition rate coefficient. *decompose_rate = ln(2)/decompose_halftime*	base	*decompose_rate*	User specified	[h^{-1}]
	The decomposition halflife.	base	*decompose_halftime*	User specified	[h]
f_C	Chemical concentration development effect on decomposition. Default no effect.	base	*decompose_conce_factor*	Empty	plf [[g cm^3 H_2O] → [-]]
f_τ	Potential lag. When reaches 1 decomposition begins. Default no effect.	base	*lag*	1	[-]

Name and explanation		Model (in Daisy)	Parameter name (Daisy reference manual)	Default	Default unit
τ	Lag increases with the value corresponding to the current concentration each hour.	base	*decompose_lag_increment*	Empty	plf [g cm^{-3} → h^{-1}]
	The decomposition processes for the soil will be used to simulate decomposition at the soil surface.	base	*soil_affects_surface_decompose*	FALSE	[-]
	The breakdown at the soil surface will generate metabolites.	base	*enable_surface_products*	FALSE	[-]
f_T	The default temperature modifier function. Follows the function for carbon when empty.	default	*decompose_heat_factor*	Empty	plf [[C°] → [-]]
T_{ref}	Reference temperature for decomposition.	default	*T_ref*	10	[C°]
f_w	The default moisture modifier function. Follows the function for carbon when empty.	default	*decompose_water_factor*	Empty	plf [[C°] → [-]]
f_z	Depth factor on decomposition. Default no effect.	default	*decompose_depth_factor*	1	plf [[cm] → [-]]
f_{CO_2}	CO_2 development factor on decomposition. Default no effect.	default	*decompose_CO2_factor*	Empty	plf [[g CO_2-C cm^{-3} h^{-1}] → [-]]
T_{ref}	Reference temperature for decomposition.	Focus	*T_ref*	20	[C°]
α	The Focus temperature effect parameter.	Focus	*alpha*	0.0948	[K^{-1}]
B	The Focus soil moisture effect parameter.	Focus	*B*	0.49	[-]

Name and explanation		Model (in Daisy)	Parameter name (Daisy reference manual)	Default	Default unit
z	The end of each depth interval used by the Focus depth modifier function.	Focus	*z*	-30 -60 -100	[cm]
f_z	Depth factor for each z interval.	Fcous	*z_factor*	1 0.5 0.3	[]
fraction	Fraction of decomposed (parent) material that becomes the specified metabolite.	base	*decompose_products fraction*	User defined	[-]
chemical	Name of the metabolite.	base	*decompose_products Chemical*	User defined	[-]
Molar mass	Molar mass of the chemical	base	*molar_mass*	User defined	[g mol^{-1}]

Original text from	A10 Daisy description	
Updated by	date	For Daisy version
Holbak, M. and Styczen, M.	2024 08 19	6.47

8.6 References

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