Sorption Kinetics in PEARL
A Flexible Approach to Parameterisation

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ABSTRACT

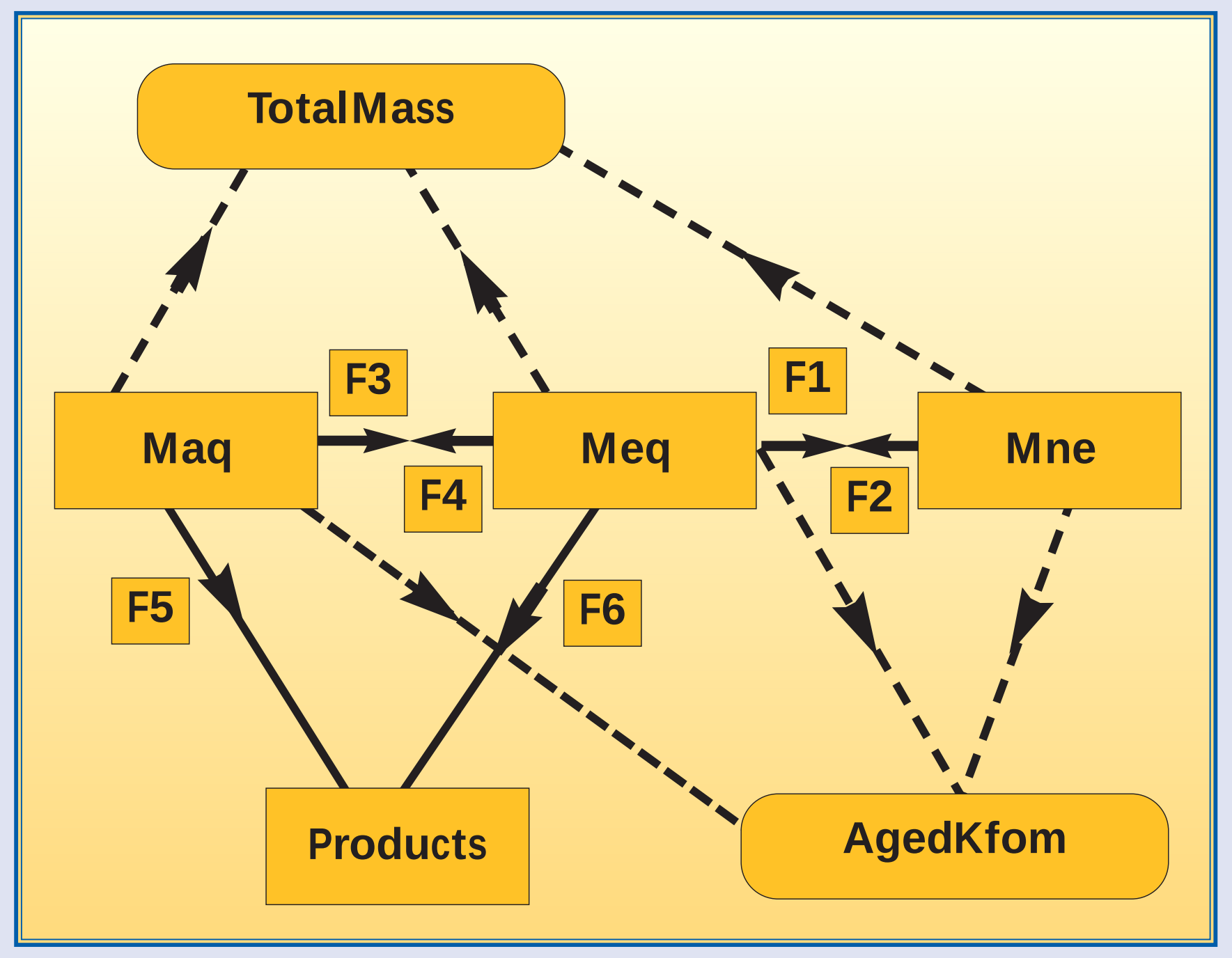
It is widely accepted that many pesticides exhibit time-dependent sorption in soil. This phenomenon leads to increased sorption and reduced availability for leaching of aged residues (1), and therefore should be considered when assessing the potential for pesticides to reach groundwater.

The PEARL leaching model has the capability to simulate sorption kinetics using a two-site representation: sorption at site 1 is an equilibrium process described by the Freundlich isotherm whereas sorption at site 2 is a non-equilibrium process described by pseudo first-order kinetics (2).

This poster describes a flexible approach to parameterisation of sorption kinetics in PEARL using a ModelMaker model together with experimental data from aged desorption studies.

METHOD

The non-equilibrium sorption sub-model in PEARL can be implemented in ModelMaker as illustrated below. A very fast adsorption rate constant is used to solve the Freundlich equation in the equilibrium sorption domain.



Compartments

Maq = mass in solution, equilibrium phase [mg]
Meq = mass on soil, equilibrium phase [mg]
Mne = mass on soil, non-equilibrium phase [mg]
TotalMass = total mass of compound in system [mg]
AgedKfom = aged adsorption K_{FOM} [L kg^{-1}]

System parameters

D = mass of soil [kg]
V = volume of solution used during incubation [L]
Mom = mass fraction of organic matter in soil
Kfom,eq = Freundlich equilibrium adsorption [L kg^{-1}]
N = Freundlich exponent for equilibrium adsorption

Dummy parameter (to solve Freundlich equation)

ka = equilibrium partitioning rate [d^{-1}]
(set very fast, e.g. 5)

Fitted parameters

M0 = initial mass of pesticide [mg]
F = ratio of non-equilibrium to equilibrium sorption
kd = desorption rate [d^{-1}]
kt = rate of degradation in equilibrium domain [d^{-1}]

Equations

F_1 = kd x F x Meq
F_2 = kd x Mne
F_3 = ka x ((D x Kfom,eq x Mom)/V^N) x Maq^N
F_4 = ka x Meq
F_5 = kt x Maq
F_6 = kt x Meq
TotalMass = Maq + Meq + Mne
AgedKfom = (Mne+Meq) x V^N/(Maq^N x D x Mom)

EXAMPLE DATA

A simulated data set from an aged desorption study will be used to illustrate the method. The dimensions of the example test system are listed in the following table.

Properties of the test system	Units	Value
D (mass soil)	kg	0.05
V (volume of solution for adsorption)	L	0.01
Vdes (total volume of solution for desorption)$^+$	L	0.05
Mom (mass fraction of soil organic matter)	-	0.02
Kfom,eq (initial Freundlich adsorption K_{FOM})	L kg^{-1}	30.0
N (Freundlich exponent = 1/n)	-	0.90

+ required for conversion between desorption and adsorption

The measured total mass, and aqueous-phase concentration following desorption, at each time-point are shown in the table below.

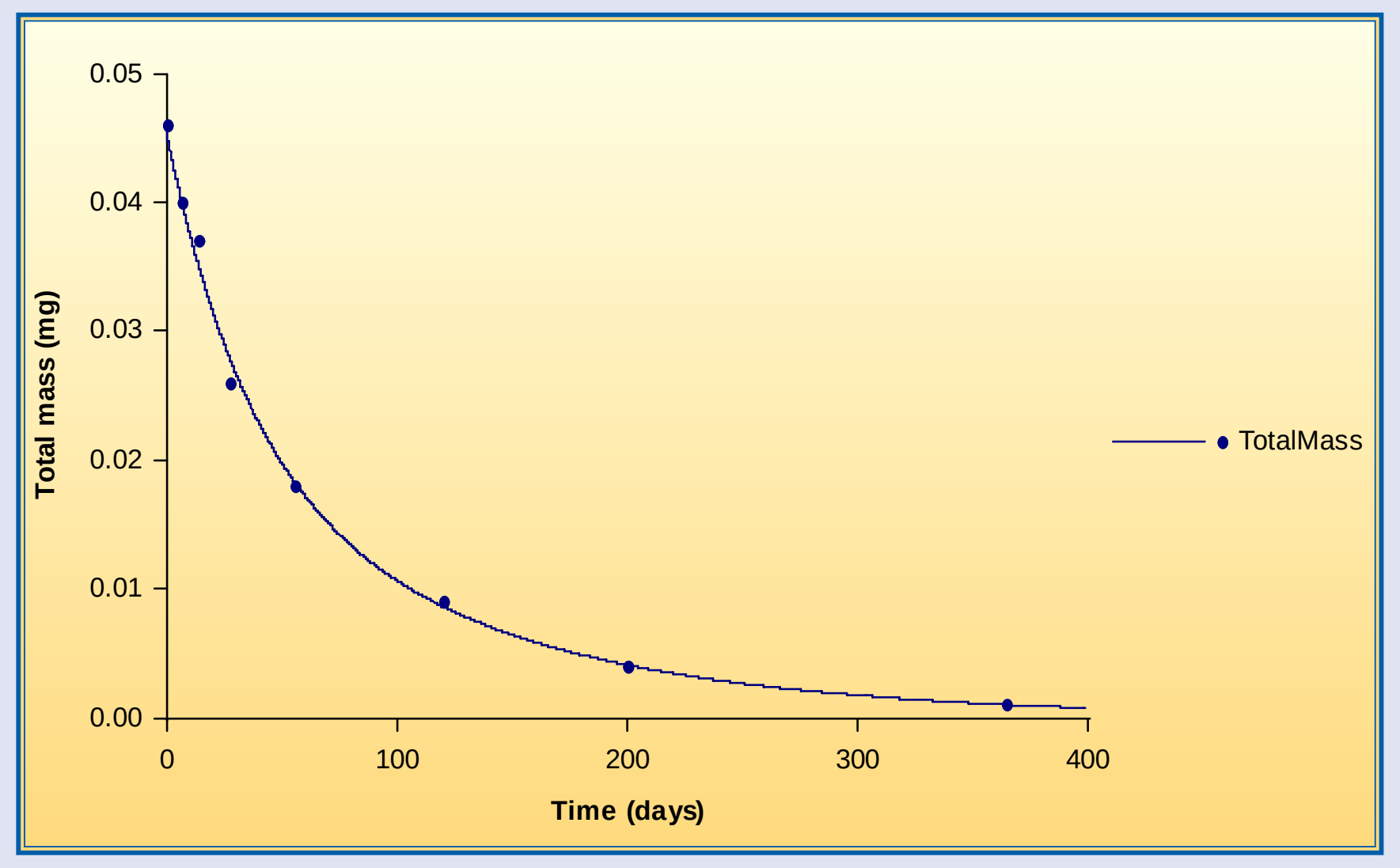
Time [days]	Example data	
	Total mass [mg]	Concentration in aqueous phase after desorption [mg L^{-1}]
0	0.046	-
7	0.040	0.472
14	0.037	0.416
28	0.026	0.273
56	0.018	0.148
120	0.009	0.052
200	0.004	0.020
365	0.001	0.004

The non-equilibrium sorption sub-model in PEARL predicts a 'hysteresis' effect, with an increasing discrepancy between adsorption and desorption coefficients over time. In order to fit the ModelMaker model, aged adsorption K_{FOM} values can be calculated by assuming that re-partitioning occurs only in the equilibrium sorption domain during the desorption step.

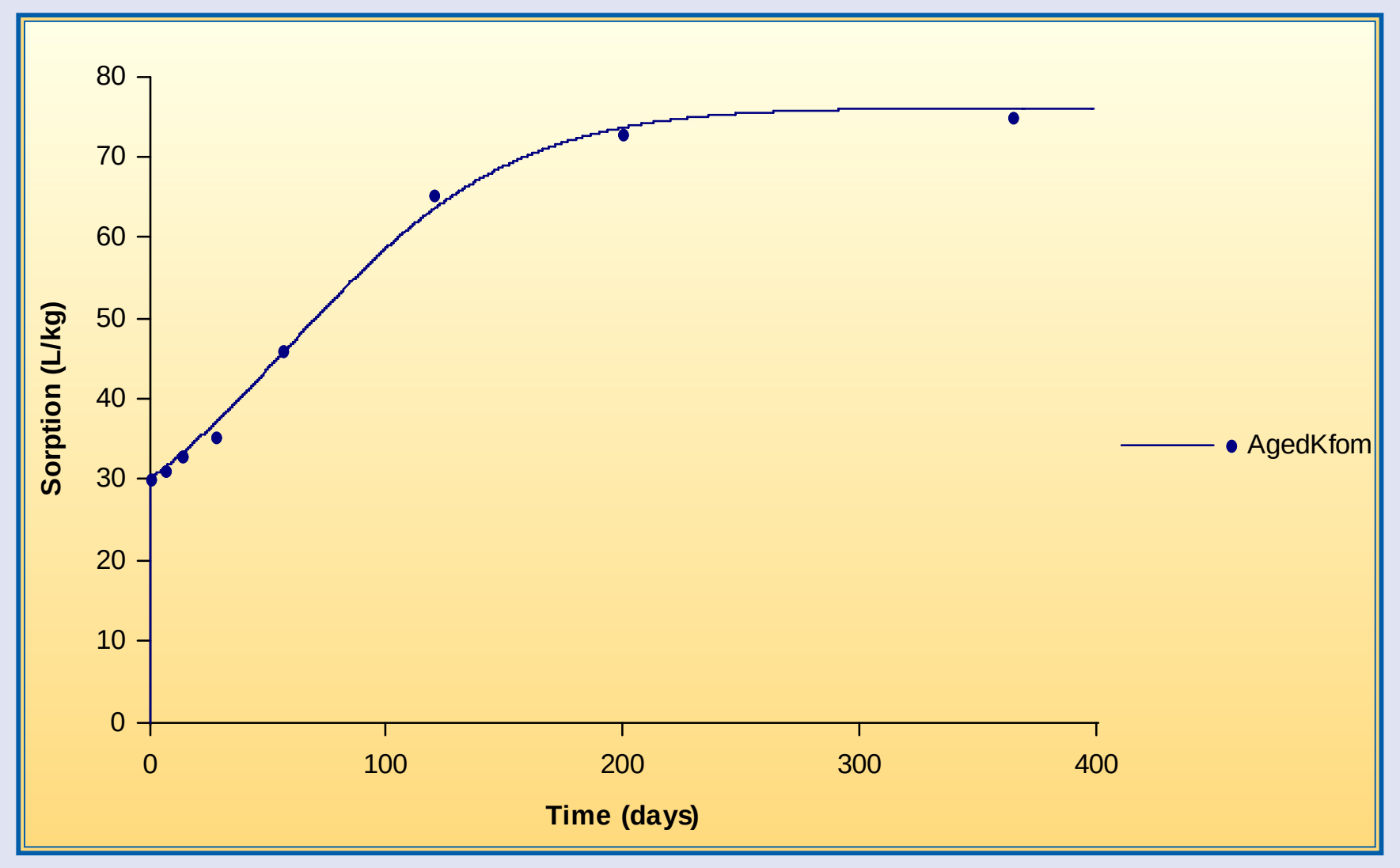
Time [days]	Measured data can be expressed as: [L kg^{-1}]		
	Desorption K_{OM}	Desorption K_{FOM}	Adsorption K_{FOM}
0	-	-	30.0
7	34.8	32.3	31.2
14	39.0	35.7	33.0
28	45.3	39.8	35.2
56	71.7	59.2	45.9
120	124.5	92.5	65.3
200	153.4	103.6	72.9
365	177.9	103.4	74.9

EXAMPLE RESULTS

The ModelMaker fits to the example data set are shown below. The optimised fits were obtained with a desorption rate constant (kd) of 0.0132 per day and a ratio of non-equilibrium to equilibrium sorption (F) of 0.558.



Degradation with time



Increase in sorption with time

The optimised half-life in the equilibrium sorption domain was 36 days. The system half-life, fitted directly to the data for total mass using single first-order kinetics, was 45 days. The effect on PEC_{GW} of implementing adsorption kinetics in PEARL is illustrated in the table below.

Scenario (20 g a.i. ha^{-1} to maize, pre-emergence)	FOCUS PEARL PEC_{GW} [µg L^{-1}]	
	Initial sorption	Time-dependent sorption
Châteaudun	0.072	0.026
Hamburg	0.091	0.039
Kremsmünster	0.070	0.031
Okehampton	0.107	0.048
Piacenza	0.168	0.085
Porto	0.001	< 0.001
Sevilla	0.010	0.004
Thiva	0.058	0.021

CONCLUSIONS

Time-dependent sorption processes can have an important influence on the potential for pesticides to leach to groundwater. This poster shows how the non-equilibrium sorption sub-model in PEARL can be implemented in ModelMaker to give a flexible, graphical tool for calibrating sorption kinetic parameters. Aged desorption studies can provide suitable experimental data for fitting the sorption kinetic parameters in PEARL.

REFERENCES

(1) Walker A, Rodriguez-Cruz MS and Mitchell MJ (2005). Influence of ageing of residues on the availability of herbicides for leaching. Environmental Pollution 133: 43 – 51.

(2) Boesten JJTI and van der Linden AMA (2001). Effect of long-term sorption kinetics on leaching as calculated with the PEARL model for FOCUS scenarios. BCPC Symposium Proceedings No. 78.

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