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SORPKINANALYSIS 1.0

Implementation of a two-site aged sorption model

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Content

1 Summary

SorpKinAnalysis is a user-friendly implementation of the two-site modelling approach of kinetic sorption comparable to PEARLNEQ (Boesten and ter Horst 2012). The approach was proposed in the scientific opinion on aged sorption studies for pesticides by EFSA PPR Panel 2018.
The software SorpKinAnalysis fulfils the requirements for a software tool given in EFSA PPR Panel 2018, pp. 24-25:
Capability
The program SorpKinAnalysis is able to calculate all parameter values of the aged sorption model. Furthermore, a statistical assessment for the goodness of fit is delivered (e.g. model efficiency). In addition to that the program SorpKinAnalysis provides a graphical representation of the fit and the residuals.
Documentation
The implementation of the aged sorption concept is described. A "Working with…" section guides through the software SorpKinAnalysis. For the assessment of goodness of fit several statistical methods are implemented (e.g. Chi²-statistics, coefficient of determination, model efficiency). The performance of SorpKinAnalysis is tested using ECPA-07 (EFSA PPR Panel 2018) as benchmark data set. Detailed output of the program is given in the appendix. SorpKinAnalysis delivers nearly identical results for aged sorption parameters for the example data set.
Compatibility
The program SorpKinAnalysis is available for major operating systems (like Windows 7-10).
Availability
The program SorpKinAnalysis is currently available free-of-charge at the software website of the Fraunhofer Institute for Molecular Biology and Applied Ecology IME. Permanently, the program and associated material is linked to the download area http://software.ime.fraunhofer.de/SorpKinAnalysis/. Earlier versions are available upon request. Here, the user can also obtain support from the developers of the software.
User interface
The user interface of SorpKinAnalysis is graphical implanted in VB.Net. No further programming skills are needed for the use of the software.
Thematic Background
The aim is to obtain input parameter values for FOCUS PEARL 4.4.4 and FOCUS PELMO 5.5.3, which are used in current groundwater leaching assessment to get a predicted environmental concentration in groundwater value (PEC_{GW}).

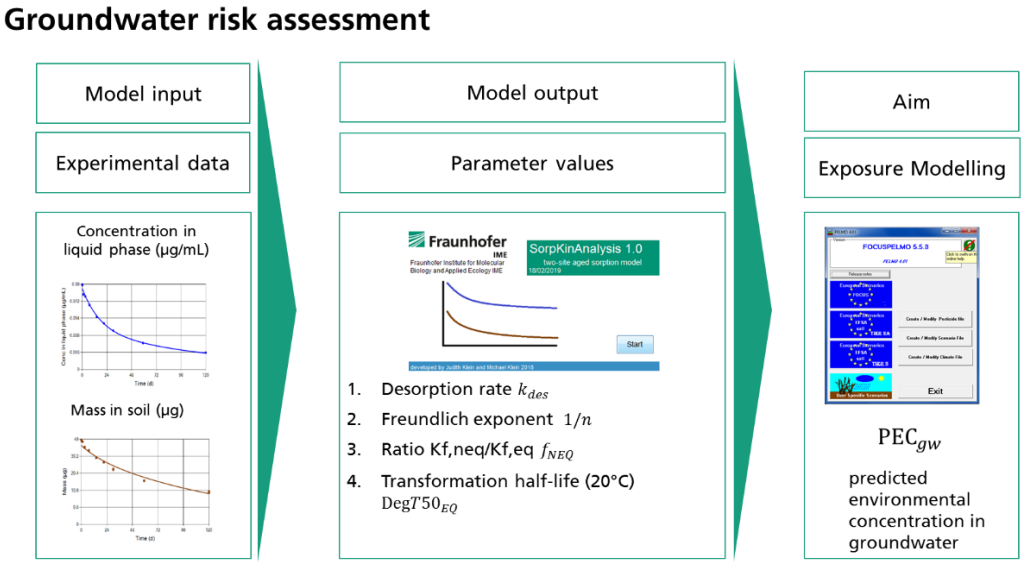

Figure 1: Schematic representation of the thematic background of SorpKinAnalysis.

2 Model description

This section is based on Appendix E in EFSA PPR Panel 2018, and Klein 2010.

The same two-site model is implemented in the leaching models PEARL and PELMO.

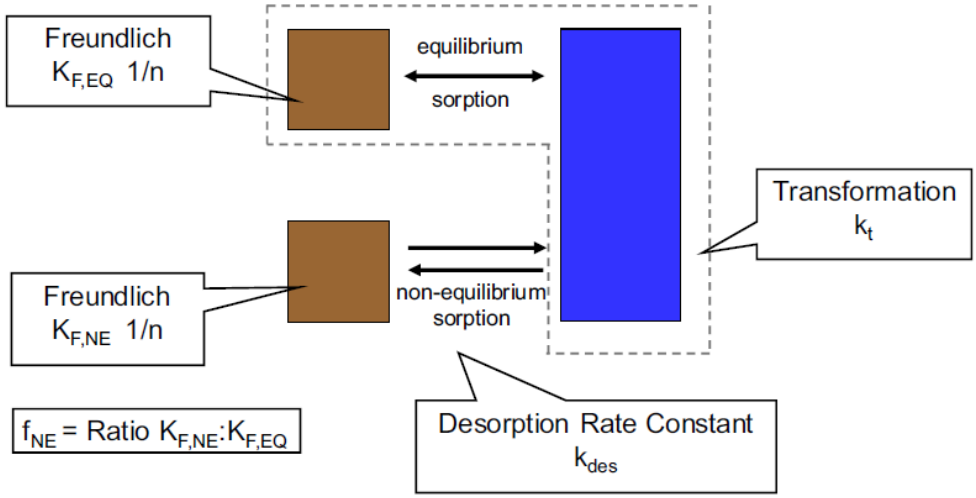

Figure 2: Schematic representation of the two-aged sorption model taken from EFSA PPR Panel 2018.

In Figure 2, the two-site aged sorption model by Leistra et al. 2001 is represented schematically. The figure is taken from EFSA PPR Panel 2018.

The assumption of the model is that sorption is instantaneous on one fraction of the sorption sites (dashed line in Figure 2). The sorption of the remaining fraction is low. The equilibrium sorption sites reach equilibrium within 24 h; the non-equilibrium sites do not reach equilibrium within 24 h (Boesten and ter Horst 2012).

Degradation is described by first-order kinetics. The model does not account for irreversible sorption.

The kinetic sorption model consists of two different kinds of model parameters:

1. system parameters, and
2. sorption/degradation parameters.

The model parameters can be seen in Table 1. For each parameter the corresponding PEARLNEQ v5 name, a reasonable range (minimal value, maximal value), unit as well as description is given. The last column in Table 1 indicates whether a parameter is fixed or is fitted.

Table 1: Parameter of the two-site aged sorption model (Leistra et al. 2001). The parameters are given with their range (minimum value, maximum value), with their unit as well as their description.

Parameter	PEARLNEQ v5	Min	Max	Unit	Description	Fit
M_0	MasIni	0	10000	µg	Initial mass of pesticide	yes
M_sol	MasSol	0	10000	g	Mass of dry soil	no
V_sol	VolLiqSol	0	10000	ml	Volume of liquid in moist soil	no
V_add	VolLiqAdd	0	10000	ml	Volume of liquid added	no
cont_OC	CntOm	0	10000	kg/kg	Organic carbon content	no
c_LR	ConLiqRef	0.1	10000	mg/l	Reference concentration	no
ExpFre	ExpFre	0.01	1.3	-	Freundlich 1/N	yes
KOC_EQ	KomEql	0	10000	l/kg	Equilibrium KOC	yes
f_NEQ	FacSorNeqEql	0	10000	-	Ratio Kf,neq/Kf,eq	yes
k_des	CofRatDes	0	0.5	1/d	Desorption rate coefficient	Yes
DT50_EQ	DT50Ref	0.1	100000	D	Transformation half-life (20°C)	yes

System properties, **Sorption/degradation parameters**

The overall aim is to use SorpKinAnalysis to get input values to be used in exposure assessment (PELMO, PEARL) for the prediction of environmental concentration in groundwater.

- DegT50eq (Transformation half-life at 20°C),
- KOC_EQ (Equilibrium KOC),
- Expfre (Freundlich coefficient 1/n)
- k_des (desorption rate coefficient),
- f_NEQ (ratio Kf,neq/Kf,eq).

In a first step, the transformation half-life $\mathrm{DT50}_{ref}$ (normalised to 20°C) is transformed to a transformation rate coefficient k_t.

$$k_t = \frac{\ln(2)}{\mathrm{DT50}_{ref}}$$

For the calculation of the total mass of pesticide in each jar, the total volume of liquid is needed. The total volume V_{liq} of liquid is the sum of volume of liquid in moist soil V_{sol} and volume of added liquid V_{add}.

$$V_{liq} = V_{sol} + V_{add}$$

The equilibrium Freundlich sorption coefficient $K_{f_{EQ}}$is calculated via the mass content, mass fraction of organic carbon in the soil (kg/kg) $cont_{OC}$ and coefficient of equilibrium sorption on organic matter (mL/g) $K_{OC_{EQ}}$.

$$K_{f_{EQ}} = cont_{OC} \cdot K_{OC_{EQ}}$$

The factor f_{NEQ} describes the ratio between the equilibrium $K_{f_{EQ}}$ and non-equilibrium $K_{f_{NEQ}}$Freundlich coefficient.

$$f_{NEQ} = \frac{K_{f_{EQ}}}{K_{f_{NEQ}}}$$

The non-equilibrium Freundlich sorption coefficient $K_{f_{NEQ}}$ can be calculated via the ratio factor f_{NEQ}.

$$K_{f_{NEQ}} = f_{NEQ} \cdot K_{f_{EQ}}$$

The total mass of pesticide in each jar (mg) M is the sum of the volume of the liquid V_{liq} multiplied with the concentration in the liquid phase (mg/L) c_{liq} and the mass of dry soil incubated in each jar (g) M_{sol} multiplied by the content sorbed at equilibrium sites X_{EQ} and non-equilibrium sites X_{NEQ} (µg/g).

$$M(t) = V_{liq} \cdot c_{liq}(t) + M_{sol} \cdot \left(X_{EQ}(t) + X_{NEQ}(t)\right)$$

For the calculation of sorption of pesticide a Freundlich sorption equation is used which describes that the partitioning between the solid and liquid phases is dependent on concentration (c_{Liq}).

$$X_{EQ}(t) = K_{f_{EQ}} \cdot c_{LR} \cdot \left(\frac{1}{c_{LR}} \cdot c_{liq}(t)\right)^{\frac{1}{N}}$$

It is not possible to solve this equation explicitly. However, the equation can be solved iteratively using the following form of the Freundlich equation:

$$\frac{X_{EQ}(t)}{c_{liq}(t)} = K_{f_{EQ}} \cdot (c_{LR})^{1-\frac{1}{N}} \cdot \left(c_{liq}(t)\right)^{\frac{1}{N}-1}$$

The content sorbed at non-equilibrium sites (µg/g) follows a first order kinetics:

$$\frac{d}{dt} X_{NEQ}(t) = k_{des} \cdot \left(X_{EQ}(t) - X_{NEQ}(t)\right), \qquad X_{NEQ}(0) = 0$$

The speed of sorption is described by desorption rate coefficient (1/d) k_{des}.

$$\frac{d}{dt} X_{NEQ}(t) = k_{des} \cdot \left(K_{f_{NE}} \cdot c_{LR} \cdot \left(\frac{c_{liq}}{c_{LR}}\right)^{\frac{1}{N}} - X_{NEQ}\right)$$

However, due to Freundlich sorption equation describing the content sorbed at equilibrium sites an analytical solution of this equation is not possible. The differential equation can be solved approximately using e.g. Euler.

The change of total mass of pesticide in each jar (µg) in time is described using a differential equation (first order kinetics). The solution of the differential equation is a function $M\colon [0, t_n] \to \mathbb{R}_+$ satisfying the initial values condition (initial mass of pesticide $M(0) = M_0$).
The speed of the process describes the degradation rate coefficient (1/d) k_t.

$$\frac{d}{dt} M(t) = -k_t \cdot \left(V_{liq} \cdot c_{liq}(t) + M_{sol} \cdot X_{EQ}(t)\right), \qquad M(0) = M_0$$

Above used additional parameters and functions are presented in summary with the respective PEARLNEQ name, unit and description in **Table 2** and **Table 3**.

Table 2: Additional parameter used in the two-site aged sorption model (Leistra et al. 2001). The parameters are given with their unit as well as their description.

Parameter	PEARLNEQ v5	Unit	Description
$K_{f_{EQ}}$	CofFreEql	mL/g	equilibrium Freundlich sorption coefficient
$K_{f_{NEQ}}$	CofFreNeq	mL/g	non-equilibrium Freundlich sorption coefficient
k_t	-	1/d	transformation rate coefficient
V_{liq}	VolLiq	mL	the volume of water in the soil incubated in each jar

Table 3: Additional functions used in the two-site aged sorption model (Leistra et al. 2001). The parameters are given with their unit as well as their description.

Function	PEARLNEQ v5	Unit	Description
$c_{liq}: [0, t_n] \rightarrow \mathbb{R}_+$	Conliq	µg/L	concentration in the liquid phase
$M: [0, t_n] \rightarrow \mathbb{R}_+$	Mas	µg	total mass of pesticide in each jar
$X_{EQ}: [0, t_n] \rightarrow \mathbb{R}_+$	XeqSus	µg/g	content sorbed at equilibrium sites
$X_{NEQ}: [0, t_n] \rightarrow \mathbb{R}_+$	Xneq	µg/g	content sorbed at non-equilibrium sites

3 Parameter fitting

The objective implemented in the software SorpKinAnalysis 1.0 is least squares: the quadratic deviation of experimental data and model prediction. This means we want to find parameter values such that the objective function value is as small as possible.

$$\min \sum_{i=1}^{n} \left(M_i - M(t_i)\right)^2 + \sum_{i=1}^{n} \left(c_{liq_i} - c_{liq}(t_i)\right)^2$$

In SorpKinAnalysis 1.0 the user can choose between various variants of least squares:

1. Unweighted least squares (all quadratic deviations are considered equally),
2. Weighted least squares
    a. The weight is equal to the mean of observations

$$\min \frac{1}{\bar{M}^2} \cdot \sum_{i=1}^{n} \left(M_i - M(t_i)\right)^2 + \frac{1}{\overline{c_{liq}}^2} \sum_{i=1}^{n} \left(c_{liq_i} - c_{liq}(t_i)\right)^2$$

    b. The weight is equal to the current observation value

$$\min \sum_{i=1}^{n} \frac{1}{M_i^2} \cdot \left(M_i - M(t_i)\right)^2 + \sum_{i=1}^{n} \frac{1}{{c_{liq}}_i^2} \left(c_{liq_i} - c_{liq}(t_i)\right)^2$$

Weights can be helpful to account for differences in absolute values.

3.1 Data requirements

For the parameterization of the model experimental data is needed: concentration of substance in liquid phase in µg/mL in time and mass of substance in soil in time in µg.

Currently no test guideline for aged sorption exists. However, soil incubation can be conducted to soil degradation study guideline OECD 307 and the batch equilibrium according to OECD guideline 106 (FOCUS 2009).

Amongst others, following supporting information is listed in EFSA PPR Panel 2018:

CRD (Chemicals Regulation Directorate), 2016. Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments. Prepared by The Food and Environmental Research Agency. Funded by Defra, UK.

ECPA (European Crop Protection Association), 2012. Opinion of the ECPA non-equilibrium sorption working group on the: 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments'.

In general, EFSA PPR Panel 2018 states that all measurements should initially be included in the optimization. Outliers can be left out if they yield a significantly better statistical correspondence between data and observation (e.g. better Chi² value).

3.2 Initial values

Parameter fitting is nothing else than solving a nonlinear optimization problem. Due to the non-linearity of the problem it is possible that there are several combinations of parameters leading in a similar objective function value (local optima). However, we are interested in a single combination of parameters that results in the smallest possible value for the merit function (global optimum).

According to EFSA PPR Panel 2018, the initial Freundlich exponent shall be set to soil-specific values obtained from OECD 106 batch experiments (OECD, 2000). The Freundlich exponent 1/n can be derived via Tier 1 batch adsorption studies.

It is possible to get DegT50 values using Tier 1 degradation studies (no $CaCl_2$ extraction). Tier 2A aged sorption studies (total mass, $CaCl_2$ extraction) can be used to get values for DegT50eq, f_NEQ, k_des.

EFSA PPR Panel 2018 suggests to test four different sets of initial values for f_NEQ (ratio Kf,neq/Kf,eq) and the desorption rate coefficient k_des (Table 4).

Table 4: Initial values recommended by EFSA PPR Panel 2018 for f_NEQ (ratio Kf,neq/Kf,eq) and k_des (desorption rate coefficient).

Parameter	1	2	3	4
f_NEQ	0.2	0.2	1.5	1.5
k_des	0.004	0.05	0.004	0.05

In order to improve the optimisation, it is possible to get an initial guess for the equilibrium KOC $K_{OC_{EQ}}$ by relating the initial concentration of pesticide in soil to the initial liquid concentration and to organic carbon content.

$$K_{OC_{EQ}} = \frac{\frac{M_0}{V_{sol}}}{c_{liq_i}} \cdot \frac{1}{cont_{OC}}$$

3.3 Solver

As objective function we minimize the sum of squares (quadratic deviation between observed and predicted data). The optimization problem is non-linear, as the objective function is quadratic and the constraints are non-linear.

As solver, SorpKinAnalysis uses the NelderMeadSolver Class by Microsoft Solver Foundation. The solver is suitable to find a local minimum or maximum for a box-constrained nonlinear function.

The implementation is based on the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

4 Evaluation

The program SorpKinAnalysis provides a statistical and visual evaluation of the output data. Visual assessment is the main tool for assessing goodness of fit (FOCUS 2006). The following criteria are recommended for a standard assessment by FOCUS 2006 to give additional information.

Procedure (following FOCUS 2006/2014)

1. Check the visual result
2. Avoid over-parametrization
3. Use realistic initial values
4. Constrain parameter ranges
5. Carry out stepwise fitting if necessary

The χ^2 statistics shall be used to assess the quality of the fit (EFSA PPR Panel 2018).

4.1 Visual assessment

According to FOCUS 2006/2014, measured and fitted data must always be presented graphically. It is suggested to plot measured concentrations and the calculated curve versus time. Furthermore, for revealing patterns of over- or under-predictions, a second plot should be made of the residuals (predicted values minus observed values). Optionally and not required for a standard assessment, a plot of measured versus calculated values can be presented. If transformed data is used, also the residuals shall be calculated based on the transformed data.

4.2 Statistical assessment

For the statistical assessment of goodness of fit, we present several criteria. In general, the statistical calculation can be done for the total data set, and separately for the single compartments in soil or liquid.

According to EFSA PPR Panel 2018, there are two options available: the weighted and the unweighted χ^2error. For the χ^2calculation the average of the replicate data should be used. The degree of freedom is equal to twice the number of time points minus the number of fitting parameters. EFSA PPR Panel 2018 recommends to use the unweighted method which is in line to FOCUS 2006.

However the statistical assessment is a guidance and not absolute cut-off criterion (FOCUS 2006). Please find in Table 5, an overview of the implemented statistical measurements in SorpKinAnalysis.

Let $N \in \mathbb{N}$ be the total number of data, $O \in \mathbb{R}_+^N$ the experimental observation and $C \in \mathbb{R}_+^N$ the corresponding calculated model prediction. The means of the data are represented by $\bar{O} \in \mathbb{R}_+^N$ respectively $\bar{C} \in \mathbb{R}_+^N$.

Table 5: Statistical measurements to compare the correspondence of model prediction and experimental data

Statistics	Formula
χ Model error (unweighted)	The number $m \in \mathbb{N}$ denotes the degrees of freedom (twice the number of time points minus number of model parameters) and let be $\alpha \in (0,1)$. Let χ^2_{tab} be the tabulated $\chi^2_{m,\alpha}$. Usually a value of $\alpha = 0.05$ is chosen. $$\epsilon = 100 \cdot \frac{1}{\bar{O}} \cdot \sqrt{\frac{1}{\chi^2_{\text{tab}}} \cdot \sum_{i=1}^{N} (C_i - O_i)^2}$$
χ Model error (weighted)	The number $m \in \mathbb{N}$ denotes the degrees of (twice the number of time points minus number of model parameters) and let be $\alpha \in (0,1)$. Let χ^2_{tab} be the tabulated $\chi^2_{m,\alpha}$. Usually a value of $\alpha = 0.05$ is chosen. $$\epsilon = 100 \cdot \sqrt{\frac{1}{\chi^2_{\text{tab}}} \cdot \sum_{i=1}^{N} \frac{1}{O_i^2} \cdot (C_i - O_i)^2}$$
Coefficient of Determination	$$r^2 = \left(\frac{\sum_{i=1}^{N} (O_i - \bar{O})(C_i - \bar{C})}{\sqrt{\sum_{i=1}^{N} (O_i - \bar{O})^2 \cdot \sum_{i=1}^{N} (C_i - \bar{C})^2}} \right)^2$$
Model efficiency	$$EF = 1 - \frac{\sum_{i=1}^{N} (C_i - O_i)^2}{\sum_{i=1}^{N} (O_i - \bar{O})^2}$$
Absolute Residuals	$$AR = \sum_{i=1}^{N} \lvert C_i - O_i \rvert$$
Squared Residuals	$$SR = \sum_{i=1}^{N} (C_i - O_i)^2$$
Scaled Root Mean Squared Error	$$SRMSE = \frac{1}{\bar{O}} \sqrt{\frac{1}{N} \sum_{i=1}^{N} (C_i - O_i)^2}$$
Scaled Total Error	$$STE = \frac{\sum_{i=1}^{N} \lvert C_i - O_i \rvert}{\sum_{i=1}^{N} O_i}$$

4.3 Regulatory endpoints

$DegT50_{EQ}$ is conceptually different from DegT50 as the aged sorption concept assumes no degradation in the non-equilibrium domain. Usually it should yield that $DegT50_{EQ}$ is smaller than DegT50 (EFSA PPR Panel 2018). The output of SorpKinAnalysis is $DegT50_{EQ.}$

Calculation of degradation time:

$$\mathrm{DegT}_x = \frac{\ln\left(\frac{100}{100-x}\right)}{k_t}$$

$$\mathrm{DegT}_{50} = \frac{\ln(2)}{k_t} \text{ and } \quad \mathrm{DegT}_{90} = \frac{\ln(10)}{k_t}.$$

The overall aim is to use SorpKinAnalysis to get input values to be used in exposure assessment (PELMO, PEARL) to predict environmental concentration in groundwater:

- DegT50eq (Transformation half-life, 20°C),
- KOC_EQ (Equilibrium KOC),
- Expfre (Freundlich coefficient 1/n)
- k_des (desorption rate coefficient),
- f_NEQ (ratio Kf,neq/Kf,eq).

5 Working with SorpKinAnalysis

The program SorpKinAnalysis is available at the software website of the Fraunhofer Institute for Molecular Biology and Applied Ecology IME. The program and associated material is linked to the download area http://software.ime.fraunhofer.de/SorpKinAnalysis/.

Please download the installer "SorpKin_setup_xxxxxxxx.exe" and follow the instructions. After installing SorpKinAnalysis successfully, the start form of the program appears (Figure 4).

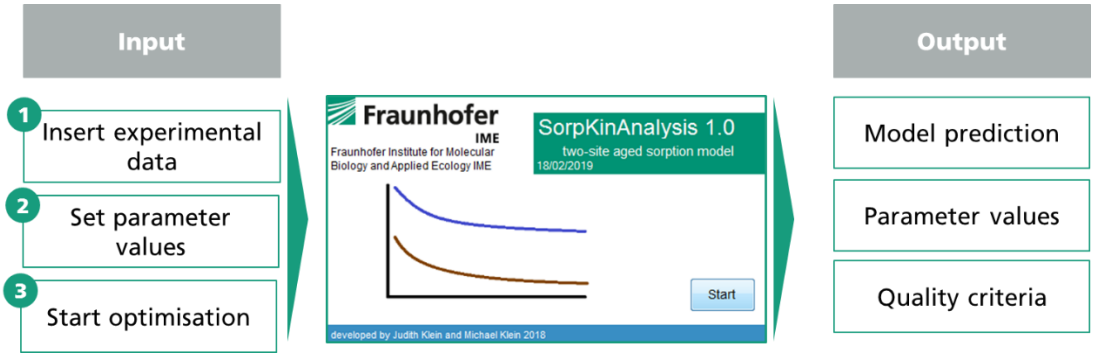

Figure 3: Schematic representation of the working procedure using SorpKinAnalysis.

For the use of SorpKinAnalysis, the user has to follow the following steps (Figure 3):

1. Enter experimental data (concentration in liquid phase, mass in soil)
2. Select settings for each parameter value (initial value, lower bound, upper bound)
3. Start the optimisation (calibration of model parameters)
4. Assess the quality of the results (statistical and graphical evaluation)

By starting the program SorpKinAnalysis, a start screen appears (Figure 4). Clicking at start the proper program is started.

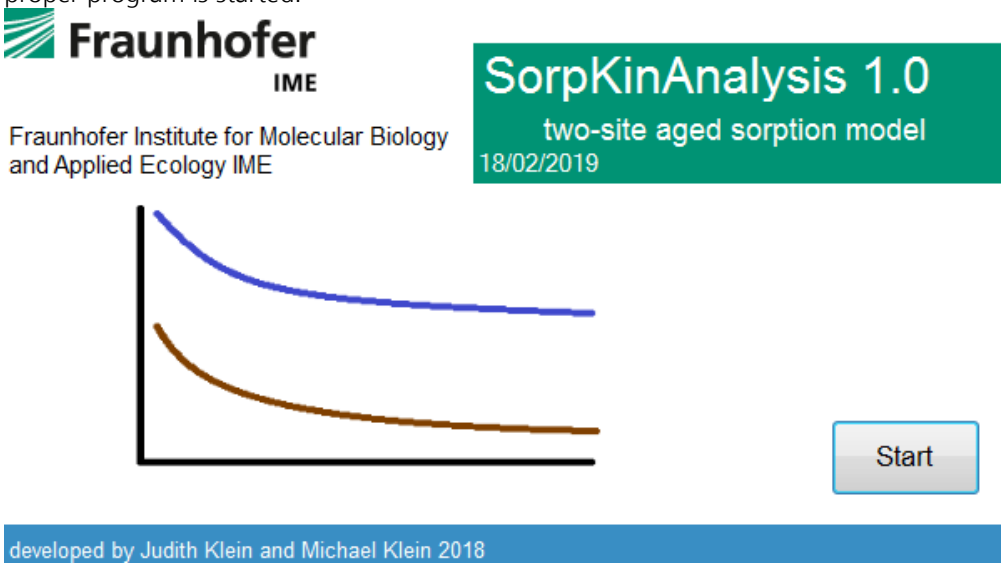

Figure 4: Start screen of the program SorpKinAnalysis

Clicking at "Start" opens the main form of SorpKinAnalysis. Here, the user has to enter the experimental data (tab page "Experimental Data") as well as information on the parameters (tab page "Parameters"). The system parameters are presented with white coloured background cells, the sorption/degradation related parameters have green coloured background cells.

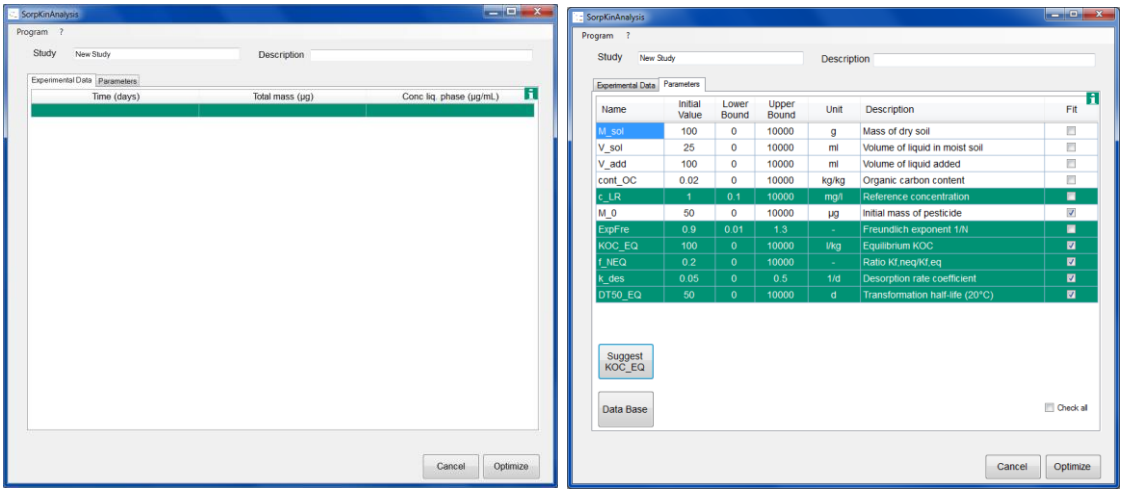

Figure 5: Main form of SorpKinAnalysis: Experimental data tab page (left) and parameters tab pages (right)

Experimental data (Figure 6) can be entered manually or by copy paste (CTRL-C,CTRL-V) from EXCEL. Fitting is only possible if experimental data is entered.

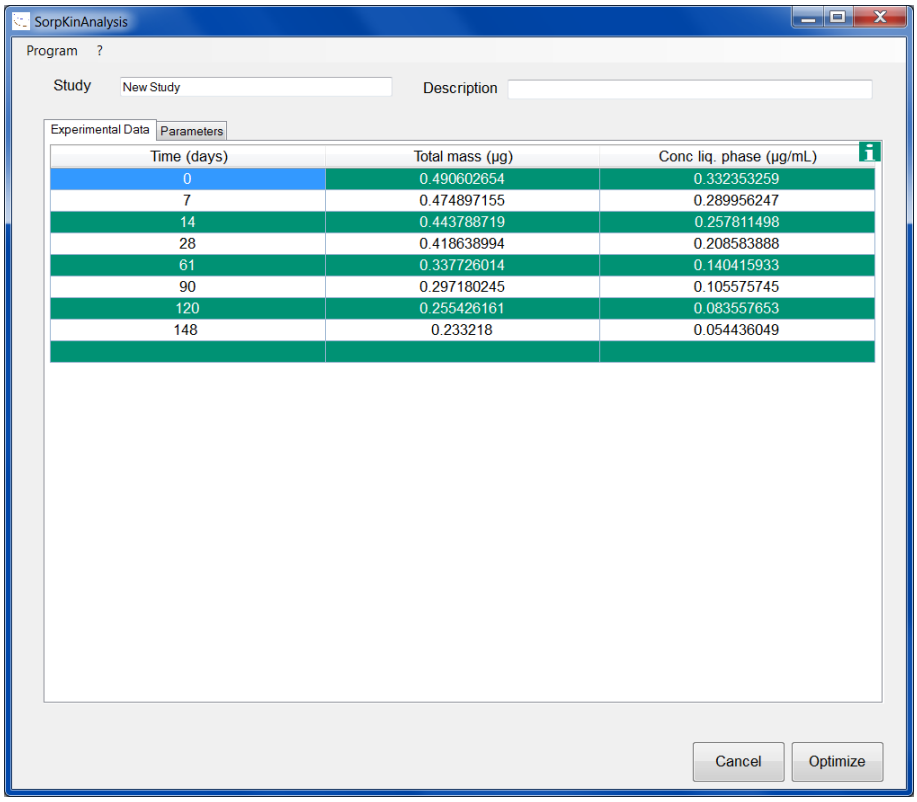

Figure 6: Experimental data in environmental residues tab page

With respect to the model parameters, the user can decide on the initial or choose values from data base, on the lower and upper bound of model parameters. Additionally, the user can decide which

parameter should be considered in the fitting routine. This enables the user to fit model parameters separately.

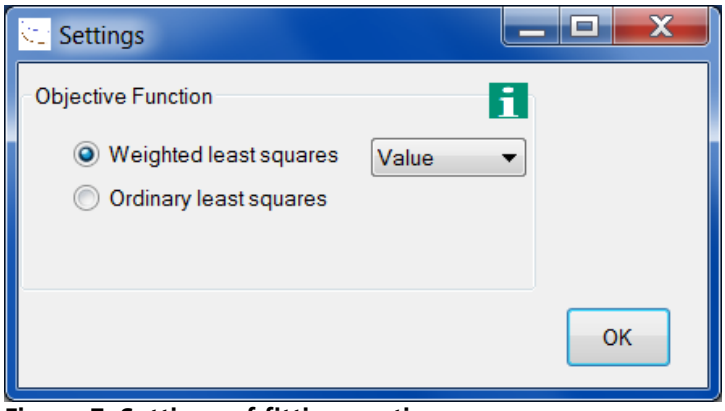

Figure 7: Settings of fitting routine

By clicking at "Options", it is possible to change the objective function (Figure 7). The default setting is the weighted least squares with a weight related to the observation at each time point. If the mass observation data is a magnitude different than the liquid data, weighted least squares possibly leads to a better fit.

The result of the optimization is represented as

1. Calibration Chart (Figure 8): Visual representation of the change of total mass of pesticide in time and the change of pesticide concentration in liquid phase.
2. Predicted-Measured Chart (Figure 9): Plot of predicted and measured data
3. Residual Chart (Figure 10): Relationship between time data and residual (predicted minus observed values)
4. Report (Figure 11): Text file containing experimental input data, model parameters (initial value, lower bound, and upper bound), result of optimization, statistical assessment.

The program enables the user to save, copy into clipboard and print the results by clicking at the menu items "Save", "Save All", "Print" and "Copy".

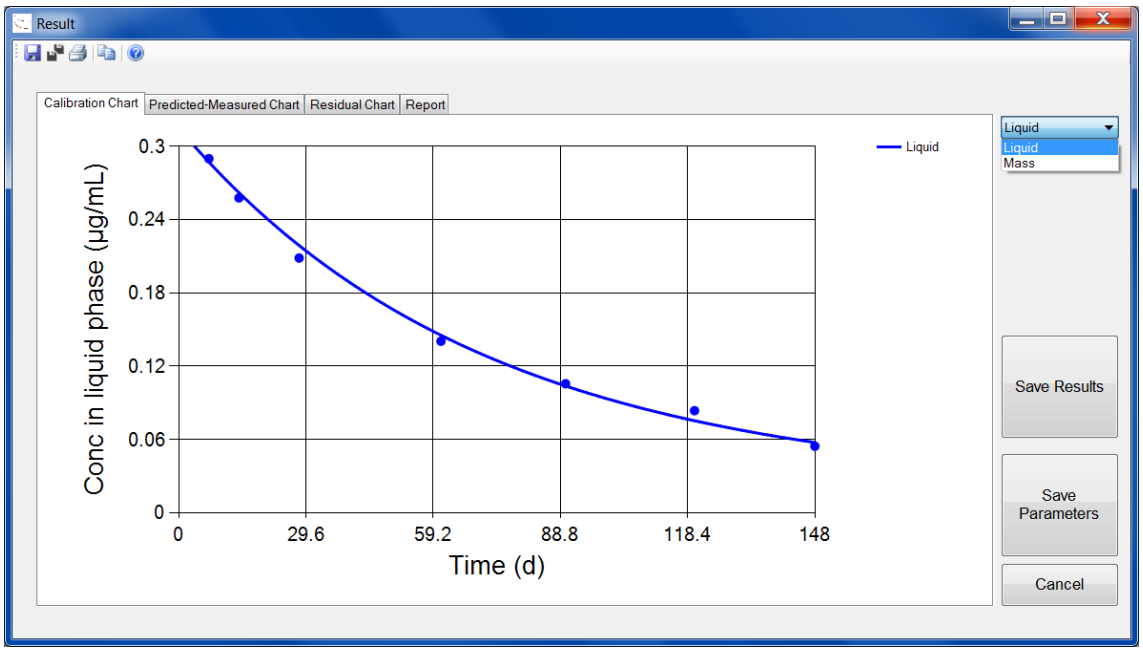

Figure 8: Graphical result of fitting, change of concentration in liquid phase (µg/mL) in time

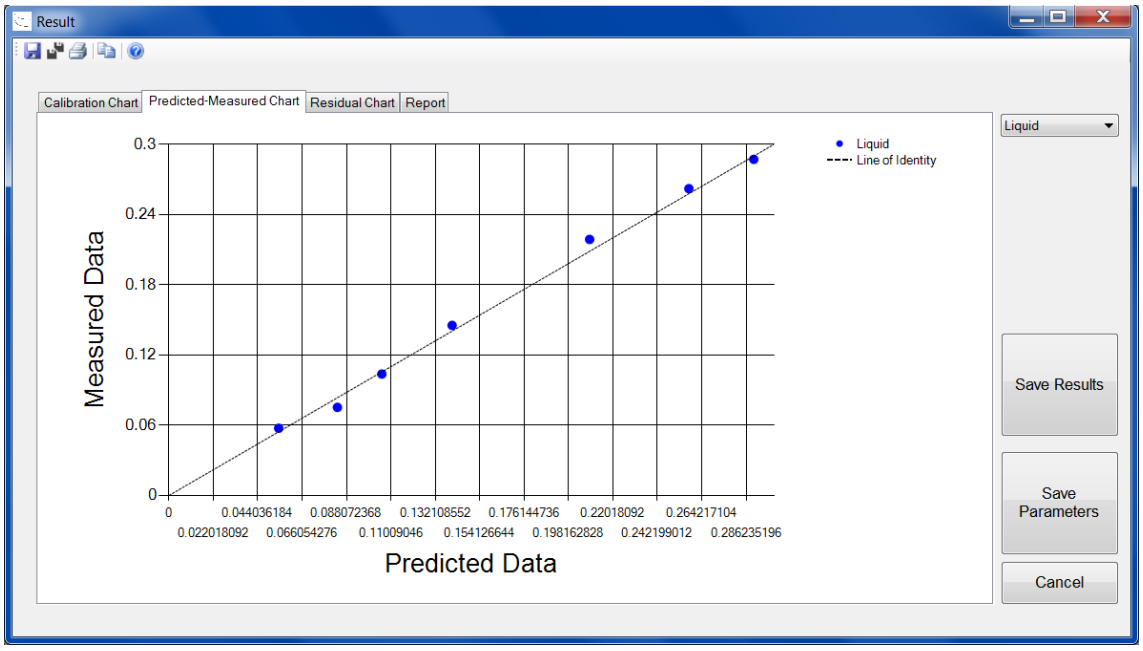

Figure 9: Predicted data versus measured data

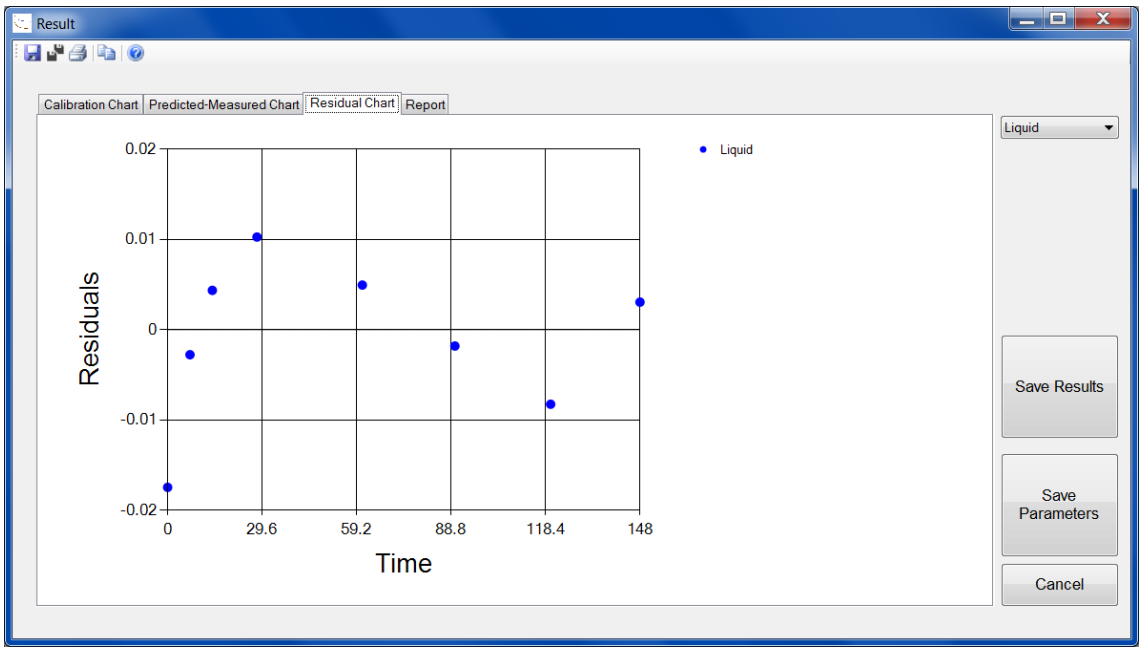

Figure 10: Time data versus residuals (predicted minus observed data)

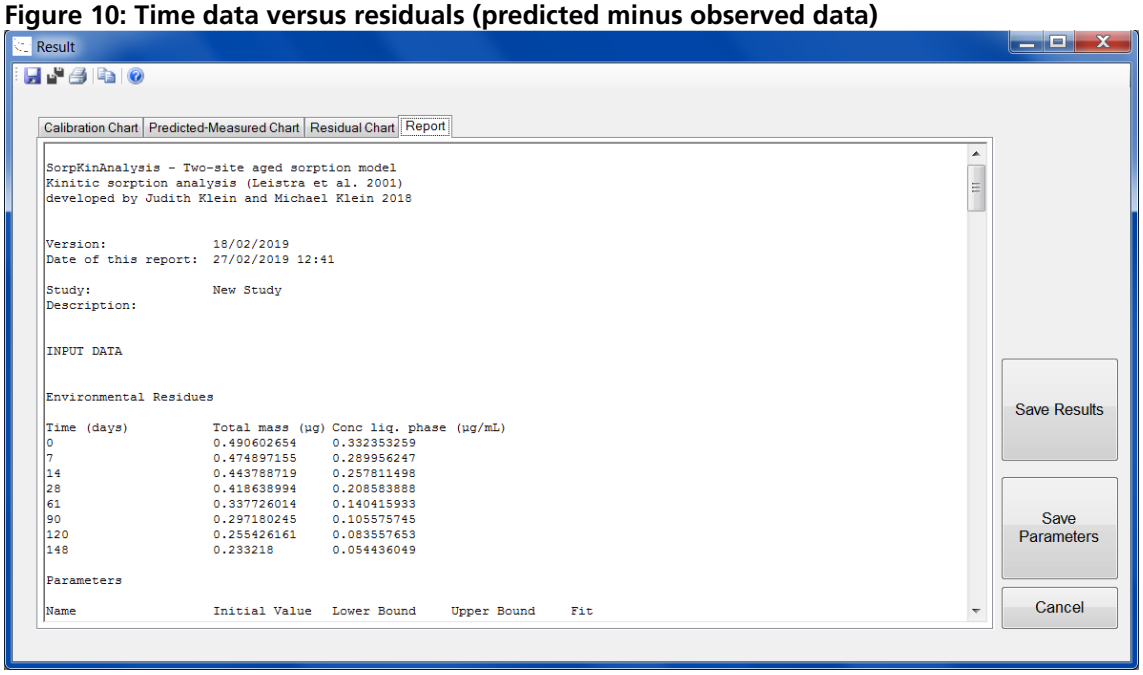

Figure 11: Text report file

Furthermore, it is possible to save the parameter values in a local data base on your computer.

6 Result of test simulations

In EFSA PPR Panel 2018 three substance ECPA-06, ECPA-07 and ECPA-01 are presented following the work flow in the draft UK guidance document.

6.1 Case Study: ECPA-01

6.1.1 Input: experimental data and (initial) parameter values

In appendix A (EFSA PPR Panel 2018), the case of pesticide ECPA-01 is presented. The study consist of different soil data: soil D, E, F and G. Table 11 contains the experimental data used for parameter fitting for each soil. Fitting is done separately for each soil.

Table 6: Experimental data, total mass in µg and concentration in liquid phase in µg/mL for ECPA-01 soil D E, F and G (EFSA PPR Panel 2018).

ECPA-01	Soil D		Soil E		Soil F		Soil G	
Time	Total mass	ConLiq	Total mass	ConLiq	Total mass	ConLiq	Total mass	ConLiq
(d)	(µg)	(µg/mL)	(µg)	(µg/mL)	(µg)	(µg/mL)	(µg)	(µg/mL)
0	7.62	0.0578	7.68	0.0600	7.44	0.0494	7.38	0.0417
0	7.62	0.0568	7.67	0.0585	7.51	0.0495	7.37	0.0419
1	7.73	0.0561	7.70	0.0580	7.21	0.0482	7.36	0.0401
1	7.64	0.0559	7.66	0.0580	7.33	0.0490	7.29	0.0399
3	7.32	0.0527	7.32	0.0536	7.20	0.0453	6.96	0.0360
3	7.35	0.0517	7.34	0.0535	7.26	0.0457	6.91	0.0361
7	6.94	0.0483	6.99	0.0507	7.16	0.0434	6.76	0.0341
7	7.09	0.0485	6.99	0.0505	6.98	0.0425	6.74	0.0339
14	6.44	0.0438	6.38	0.0454	6.39	0.0395	6.35	0.0302
14	6.40	0.0435	6.38	0.0455	6.72	0.0399	6.28	0.0305
30	5.58	0.0354	5.41	0.0364	6.03	0.0352	5.40	0.0263
30	5.53	0.0361	5.43	0.0362	6.01	0.0355	5.39	0.0257
58	4.56	0.0275	4.01	0.0255	5.43	0.0293	4.67	0.0209
58	4.57	0.0271	4.03	0.0259	5.58	0.0299	3.85	0.0212
120	3.36	0.0190	2.43	0.0147	4.64	0.0229	3.82	0.0153
120	3.30	0.0188	2.48	0.0147	4.66	0.0231	3.85	0.0154

All model parameters for the respective soils are given in Table 12. The parameters are characterized as fixed model parameter or fitting parameter. For the fitting parameter the given parameter corresponds to the initial parameter value.

Table 7: (Initial) parameter values for calibration of ECPA-01 soil D E, F and G (EFSA PPR Panel 2018).

Parameter	ECPA-01				Unit	Fit
	Soil D	Soil E	Soil F	Soil G		
M_sol	100	100	100	100	g	False
V_sol	27.7	38.2	41.95	30.25	mL	False
V_add	72.3	61.8	58.05	69.75	mL	False
cont_OC	0.025 (0.043)^	0.040 (0.067)^	0.026 (0.069)^	0.038 (0.046)^	kg/kg	False
c_LR	1	1	1	1	mg/l	False
M_0	8.042	8.042	8.042	8.042	µg	True
ExpFre	0.91	0.9	0.9	0.94	-	False
KOC_EQ	3.363	8.125	8.125	4.196	L/kg	True
f_NEQ	0.2	0.2	0.2	0.2	-	True
k_des	0.05	0.05	0.05	0.05	1/d	True
DT50_EQ	90	134	64	212	d	True

^ Numbers in bracket refer to the organic matter content (CONT_OC = CONT_OM/1.742)

6.1.2 Result using SorpKinAnalysis 1.0

The numeric parameter value result can be seen in Table 13. Each soil D-G was fitted separately. The objective function is based on weighted least squares of observed data and by model predicted data. The weight for each data point is equal to (1/observation) ².

Table 8: Parameter values of fitted model parameters of ECPA-01 soil D E, F and G (EFSA PPR Panel 2018) using SorpKinAnalysis 1.0 and the result given in EFSA PPR Panel 2018.

ECPA-01					
Parameter	**Soil D**	**Soil E**	**Soil F**	**Soil G**	**Input Exposure Modelling (geometric mean)**
M_0	7.344 (7.3)	7.51 (7)	7.191 (7.5)	6.911 (7.2)	- -
ExpFre	0.91 (0.91)	0.9 (0.9)	0.9 (0.91)	0.94 (0.91)	0.913* (0.9075)*
KOC_EQ	8.983 (9.058)	5.317 (13.065)	13.384 (8.362)	14.968 (9.407)	9.89 (9.82)
KOM_EQ	5.157 (5.2)	3.052 (7.5)	7.683 (4.8)	8.592 (5.4)	5.68 (5.64)
f_NEQ	0.582 (0.58)	0.493 (0.49)	0.512 (0.44)	0.442 (0.52)	0.5 (0.5)
k_des	0.05 (0.05)	0.044 (0.078)	0.049 (0.043)	0.074 (0.048)	0.05 (0.05)
DT50_EQ	79.46 (79.5)	60.79 (99.7)	142.775 (60.7)	92.572 (143)	89.39 (91.07)
Model error (Chi²)	4.995	2.968	3.854	7.962	-
Weighted ME (Chi²)	2.802	1.927	2.164	4.958	-

*arithmetic mean
^organic matter content (KOC_EQ = KOM_EQ/1.742)
Numbers in bracket refer to the result given in EFSA PPR Panel 2018

The fitted parameter values are very similar to the parameter values given in table B.9 in EFSA PPR Panel 2018. The number in the bracket in the cell of KOC refer to the organic matter content, which is given in EFSA PPR Panel 2018. The given statistics (model error Chi²) in Table 13 indicate a good correspondence of model prediction and experimental data.

According to EFSA PPR Panel 2018, page 18, for the use in exposure modelling, the mean of the values of all soils shall be taken:

1. Geometric mean: DT50_EQ, f_NEQ, k_des, KOC_EQ
2. Arithmetic mean: ExpFre

6.2 Case Study: ECPA-06

In appendix B in EFSA PPR Panel 2018, the case of pesticide ECPA-06 is presented. The study consist of different soil data: soil A, B, C, and D. Table 11 contains the experimental data used for parameter fitting for each soil. Fitting is done separately for each soil.

6.2.1 Input: experimental data and (initial) parameter values

ECPA-06	Soil A		Soil B		Soil C		Soil D	
Time	Total mass	ConLiq	Total mass	ConLiq	Total mass	ConLiq	Total mass	ConLiq
(d)	(µg)	(µg/mL)	(µg)	(µg/mL)	(µg)	(µg/mL)	(µg)	(µg/mL)
0	66.08	0.0695	62.54	0.0784	66.2606	0.0633	64.07	0.0569
0	66.74	0.0703	62.98	0.0802	68.4234	0.0654	65.39	0.0569
1	67.31	0.0623	61.15	0.0693	68.2351	0.0608	63.97	0.0533
1	67.01	0.0641	62.69	0.0729	69.1142	0.0622	68.27	0.0546
3	67.56	0.0604	59.19	0.0672	66.0024	0.0547	62.64	0.0499
3	67.27	0.0597	60.43	0.0661	64.4186	0.0551	63.46	0.0493
8	64.49	0.0524	59.54	0.0608	64.6907	0.0502	61.61	0.0444
8	65.29	0.0534	58.39	0.0606	63.7837	0.0498	61.58	0.0438
14	65.04	0.0462	62.10	0.0584	68.6397	0.0470	62.31	0.0443
14	65.69	0.0462	61.99	0.0586	67.9560	0.0468	63.51	0.0423
28	56.52	0.0349	51.80	0.0446	60.4976	0.0389	53.55	0.0291
28	58.85	0.0377	52.38	0.0451	59.6673	0.0390	53.35	0.0301
58	51.21	0.0278	45.46	0.0342	54.0438	0.0321	46.00	0.0221
58	51.43	0.0291	43.69	0.0314	55.0206	0.0313	43.88	0.0210
120	41.26	0.0222	34.03	0.0236	47.4785	0.0279	33.06	0.0148
120	42.27	0.0229	32.92	0.0211	50.9740	0.0309	33.09	0.0149

All model parameters for the respective soils are given in Table 12. The parameters are characterized as fixed model parameter or fitting parameter. For the fitting parameter the given parameter corresponds to the initial parameter value.

Table 9: (Initial) parameter values for calibration of ECPA-06 soil A, B, C and D (EFSA PPR Panel 2018, table B.5, B.7).

Parameter	ECPA-06				Unit	Fit
	Soil A	Soil B	Soil C	Soil D		
M_sol	100	100	100	100	g	False
V_sol	25.1	28.6	31.6	36.9	mL	False
V_add	400	400	400	400	mL	False
cont_OC	0.013 (0.0219)^	0.011 (0.0193)^	0.015 (0.0265)^	0.018 (0.031)^	kg/kg	False
c_LR	1	1	1	1	mg/l	False
M_0	68.43	64.67	69.77	66.96	µg	True
ExpFre	0.895	0.92	0.974	0.908	-	False
KOC_EQ	104.076	88.117	124.053	99.656	l/kg	True
f_NEQ	0.2	0.2	0.2	0.2	-	True
k_des	0.004	0.004	0.004	0.004	1/d	True
DT50_EQ	162	128	239	115	d	True

^ Numbers in bracket refer to the organic matter content (CONT_OC = CONT_OM/1.742)

6.2.2 Result using SorpKinAnalysis 1.0

The numeric parameter value result can be seen in Table 13. Each soil A-D was fitted separately. The objective function is based on weighted least squares of observed data and by model predicted data. The weight for each data point is equal to (1/observation) ².

Table 10: Parameter values of fitted model parameters of ECPA-06 soil A, B, C and D (EFSA PPR Panel 2018) using SorpKinAnalysis 1.0 and the result given in EFSA PPR Panel 2018.

ECPA-06					
Parameter	**Soil A**	**Soil B**	**Soil C**	**Soil D**	**Input Exposure Modelling (geometric mean)**
M_0	67.642 (-)	63.072 (-)	67 (-)	65.946 (-)	- -
ExpFre	0.895 (0.895)	0.92 (0.882)	0.974 (0.974)	0.908 (0.908)	0.924* (0.915)*
KOC_EQ	335.299 (346.658)	312.575 (346.658)	396.421 (346.658)	318.403 (346.658)	339.14 (346.66)
KOM_EQ	192.479 (199)	179.435 (161)	227.567 (224)	182.78 (185)	194.68 (190.89)
f_NEQ	0.705 (0.706)	0.605 (0.576)	0.598 (0.598)	0.668 (0.668)	0.64 (0.63)
k_des	0.04 (0.0394)	0.024 (0.0253)	0.046 (0.0456)	0.028 (0.0278)	0.03 (0.03)
DT50_EQ	107.804 (108)	90.196 (91.4)	175.792 (176)	78.683 (78.7)	107.69 (108.13)
Model error (Chi²)	2.665	4.413	4.142	3.486	-
Weighted ME (Chi²)	1.787	2.92	2.882	2.89	-

*arithmetic mean
^organic matter content (KOC_EQ = KOM_EQ/1.742)
Numbers in bracket refer to the result given in EFSA PPR Panel 2018

The fitted parameter values are very similar to the parameter values given in table B.9 in EFSA PPR Panel 2018. The number in the bracket in the cell of KOC refer to the organic matter content, which is given in EFSA PPR Panel 2018. The given statistics (model error Chi²) in Table 13 indicate a good correspondence of model prediction and experimental data.

According to EFSA PPR Panel 2018, page 18, for the use in exposure modelling, the mean of the values of all soils shall be taken:

3. Geometric mean: DT50_EQ, f_NEQ, k_des, KOC_EQ
4. Arithmetic mean: ExpFre

6.3 Case Study: ECPA-07

6.3.1 Input: experimental data and (initial) parameter values

In appendix C.2.2 in EFSA PPR Panel 2018, the case of pesticide ECPA-07 is presented. The study consist of different soil data: soil A, B, C and D. Table 11 contains the experimental data used for parameter fitting for each soil. Fitting is done separately for each soil.

Table 11: Experimental data, total mass in µg and concentration in liquid phase in µg/mL for ECPA-07 soil A, B, C and D (EFSA PPR Panel 2018).

ECPA-07	Soil A		Soil B		Soil C		Soil D	
Time (d)	Total mass (µg)	ConLiq (µg/mL)	Total mass (µg)	ConLiq (µg/mL)	Total mass (µg)	ConLiq (µg/mL)	Total mass (µg)	ConLiq (µg/mL)
0	48.21	0.0887	47.84	0.0815	47.79	0.0661	46.97	0.0537
0	48.64	0.0897	47.81	0.0818	47.83	0.0657	46.57	0.0544
1	47.68	0.0793	46.81	0.0714	48.66	0.0595	44.20	0.0503
1	47.54	0.0789	48.11	0.0707	48.69	0.0562	45.67	0.0491
3	44.25	0.0769	45.26	0.0729	46.08	0.0549	45.37	0.0487
3	44.46	0.0771	45.56	0.0734	46.31	0.0561	44.87	0.0490
7	42.17	0.0677	42.67	0.0662	44.39	0.0494	43.21	0.0436
7	42.64	0.0683	43.24	0.0670	44.61	0.0487	43.20	0.0437
14	38.27	0.0559	38.29	0.0542	41.36	0.0411	37.97	0.0365
14	38.60	0.0554	39.19	0.0560	41.32	0.0412	38.30	0.0364
21	35.72	0.0487	34.53	0.0478	40.11	0.0361	34.26	0.0314
21	35.95	0.0485	35.04	0.0493	39.78	0.0369	33.96	0.0321
30	31.44	0.0411	30.38	0.0408	37.22	0.0329	31.69	0.0269
30	31.89	0.0411	30.76	0.0414	37.31	0.0326	31.73	0.0270
59	25.05	0.0277	21.01	0.0250	31.63	0.0237	22.90	0.0170
59	25.03	0.0281	21.94	0.0264	31.80	0.0238	23.42	0.0168
120	18.98	0.0177	11.26	0.0124	25.39	0.0164	14.31	0.0089
120	18.28	0.0178	11.37	0.0131	25.05	0.0178	14.50	0.0089

All model parameters for the respective soils are given in Table 12. The parameters are characterized as fixed model parameter or fitting parameter. For the fitting parameter the given parameter corresponds to the initial parameter value.

Table 12: (Initial) parameter values for calibration of ECPA-07 soil A, B, C, and D (EFSA PPR Panel 2018).

Parameter	ECPA-07				Unit	Fit
	Soil A	Soil B	Soil C	Soil D		
M_sol	100	100	100	100	G	False
V_sol	23.2	29.6	31.4	45.9	mL	False
V_add	376.8	370.4	368.6	354.1	mL	False
cont_OC	0.012 (0.021)^	0.018 (0.031)^	0.023 (0.04)^	0.046 (0.079)^	kg/kg	False
c_LR	1.0	1.0	1.0	1.0	mg/l	False
M_0	50.22	50.22	50.22	50.22	µg	True
ExpFre	0.845	0.868	0.864	0.865	-	False
KOC_EQ	98.9	92.2	107	74.9	L/kg	True
f_NEQ	0.2	0.2	0.2	0.2	-	True
k_des	0.05	0.05	0.05	0.05	1/d	True
DT50_EQ	171.4	54	157.5	50.4	D	True

^ Numbers in bracket refer to the organic matter content (CONT_OC = CONT_OM/1.742)

6.3.2 Result using SorpKinAnalysis 1.0

The numeric parameter value result can be seen in Table 13. Each soil A-D was fitted separately. The objective function is based on weighted least squares of observed data and by model predicted data. The weight for each data point is equal to (1/observation) ².

Table 13: Parameter values of fitted model parameters of ECPA-07 soil A, B, C, and D (EFSA PPR Panel 2018) using SorpKinAnalysis 1.0 and the result given in EFSA PPR Panel 2018.

Parameter	Soil A	Soil B	Soil C	Soil D	Input Exposure Modelling (geometric mean)
M_0	45.580 (45.375)	47.179 (47.037)	47.100 (46.902)	46.087 (45.759)	- -
ExpFre	0.845 (0.845)	0.868 (0.868)	0.864 (0.864)	0.865 (0.865)	0.861* (0.861)*
KOC_EQ	74.243 (74.328)	77.279 (81.289)	98.806 (106.534)	64.680 (69.459)	77.82 (81.77)
KOM_EQ	129.331 (129.479)	134.620 (141.605)	172.120 (185.582)	112.672 (120.998)	135.55 (142.45)
f_NEQ	0.754 (0.752)	0.334 (0.313)	0.749 (0.698)	0.516 (0.473)	0.559 (0.53)
k_des	0.033 (0.032)	0.040 (0.037)	0.041 (0.037)	0.032 (0.027)	0.036 (0.033)
DT50_EQ	55.108 (55.692)	44.619 (45.41)	77.023 (80.962)	48.065 (50.199)	54.928 (56.621)
Model error (Chi²)	5.775	2.141	3.314	3.15	-
Weighted ME (Chi²)	3.467	2.611	3.792	4.228	-

*arithmetic mean
^organic matter content (KOC_EQ = KOM_EQ/1.742)
Numbers in bracket refer to the result given in EFSA PPR Panel 2018

The fitted parameter values are very similar to the parameter values given in EFSA PPR Panel 2018. The number in the bracket in the cell of KOC refer to the organic matter content, which is given in EFSA PPR Panel 2018. The given statistics (model error Chi²) in Table 13 indicate a good correspondence of model prediction and experimental data.

According to EFSA PPR Panel 2018, page 18, for the use in exposure modelling, the mean of the values of all soils shall be taken:

5. Geometric mean: DT50_EQ, f_NEQ, k_des, KOC_EQ
6. Arithmetic mean: ExpFre

In Figure 12 to Figure 19, the visual result of calibration is presented. For each soil, the change of concentration in liquid phase in time as well as the change of mass in time is illustrated. In addition to that the residuals of these two state variables are calculated and presented in a residual plot showing the residual values in time.

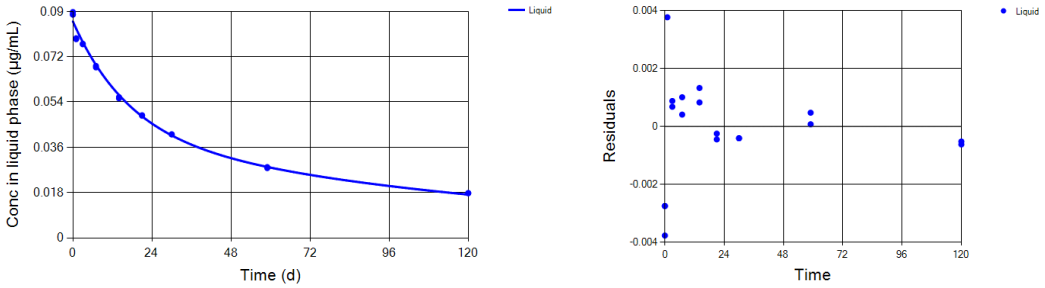

Figure 12: Soil A - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

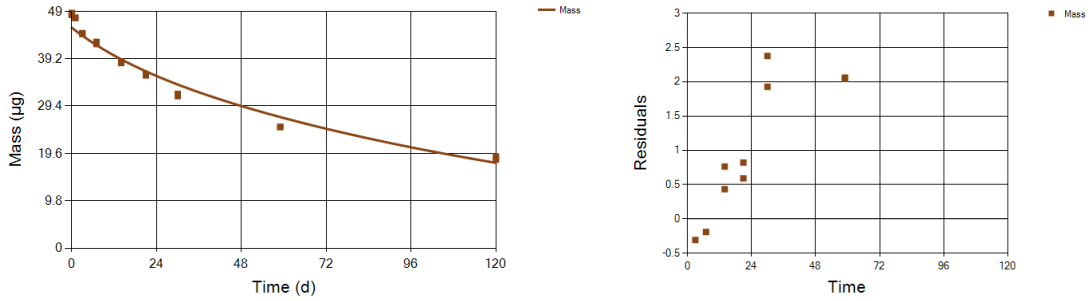

Figure 13: Soil A - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

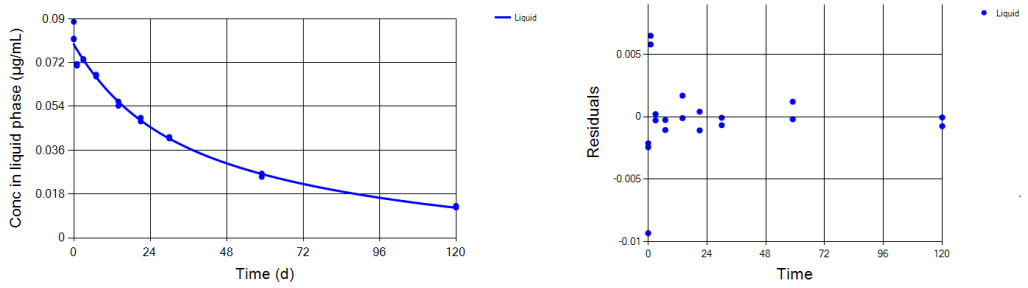

Figure 14: Soil B - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

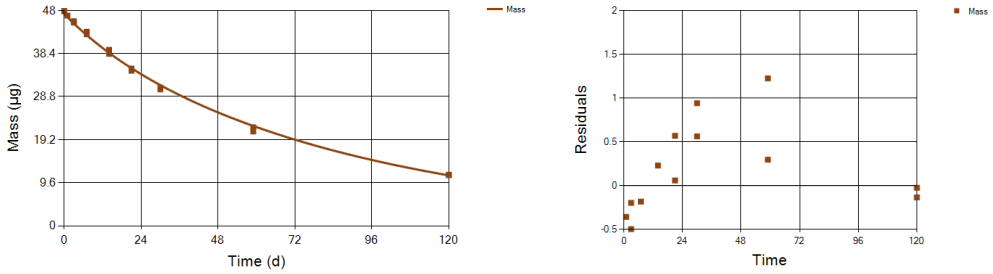

Figure 15: Soil B - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

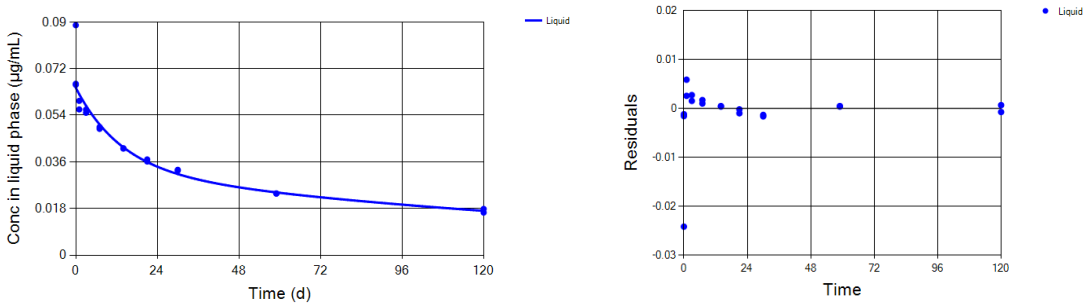

Figure 16: Soil C - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

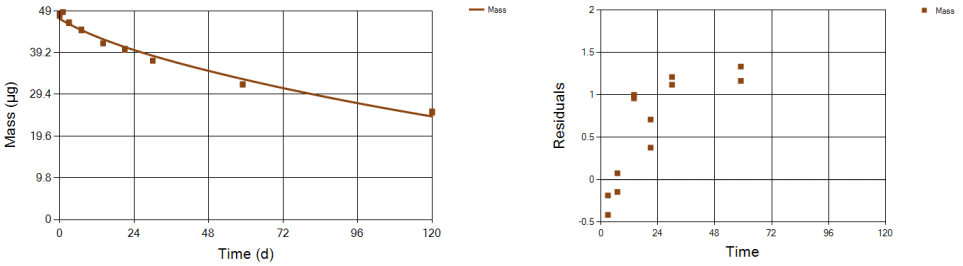

Figure 17: Soil C - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

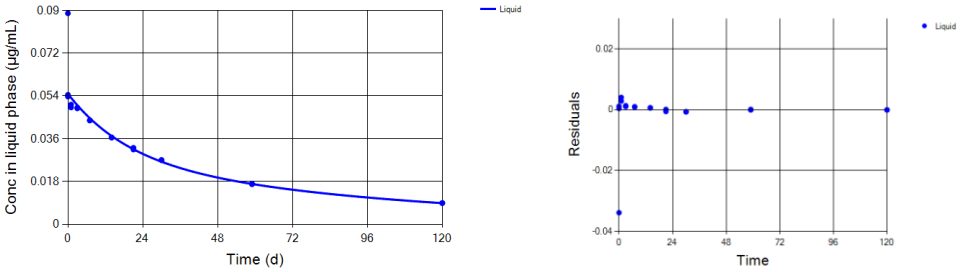

Figure 18: Soil D - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

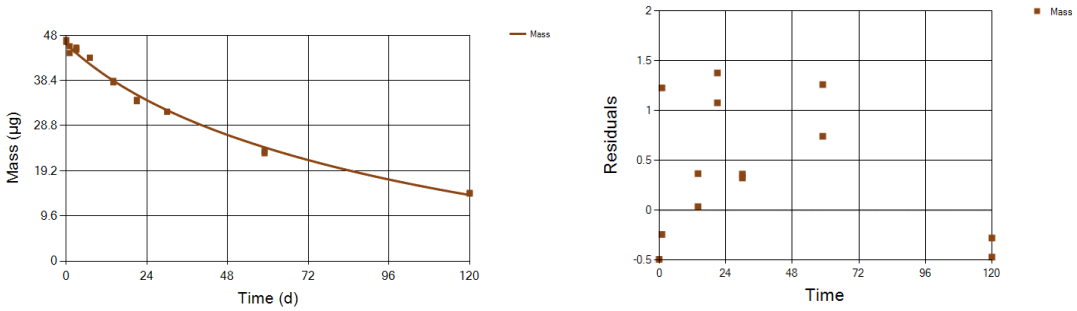

Figure 19: Soil D - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

The report created by the program SorpKinAnalysis is presented in the appendix A.1.

7 References

Boesten, J.J.T.I and M.M.S. ter Horst (2012). "Manual of PEARLNEQ v5". Working document 305. Wettelijke Onderzoekstaken Natuur & Milieu, Wageningen.

CRD (Chemicals Regulation Directorate), 2016. Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments. Prepared by The Food and Environmental Research Agency. Funded by Defra, UK.

ECPA (European Crop Protection Association), 2012. Opinion of the ECPA non-equilibrium sorption working group on the: 'Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments'.

EFSA PPR Panel (2018). "Scientific Opinion about the Guidance of the Chemical Regulation Directorate (UK) on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments". EFSA Journal 2018;16(8):5382, 86 pp. https://doi.org/10.2903/j.efsa.2018.5382

FOCUS (2006) "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration" Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.

FOCUS (2014): "Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration". Version 1.1. 18 December 2014

Gurney, A.J.R. and Hayes, S.E. 2007. Non-equilibrium sorption and degradation of pesticides in soil: analysis of laboratory aged sorption data using ModelMaker. In: A.A.M. Del Re, E. Capri, G. Gragoulis, and M. Trevisan, eds. Environmental Fate and Ecological Effects of Pesticides (Proceedings of the XIII Symposium Pesticide Chemistry). La Goliardica Pavese, Pavia Italy, ISBN 978-88-7830-473-4, pp. 245-253.

Klein M. (2010) "Calculation of rates constants according to FOCUS degradation kinetics using DegKinManager and ModelMaker". Report version 29 November 2010

Leistra, M., A.M.A. van der Linden, J.J.T.I. Boesten, A.Tiktak, and F. van den Berg (2001). "Pearl model for pesticide behaviour and emissions in soil-plant system; Description of the processes in FOCUS PEARL v 1.1.1". Bilthoven, National Institute of Public Health and the Environment. Wageningen, Alterra, Green World Search. RIVM report 711401009/Alterra-rapport 013; 116 blz.; 9 fig,: 1 tab., 42 ref.

OECD (Organisation for Economic Co-operation and Development), 2000. OECD guideline for the testing of chemicals: adsorption–desorption using a batch equilibrium method. OECD Guideline 106. OECD, Paris.

A Supplementary material

A.1 Documentation of model output: SorpKinAnalysis 1.0

A.1.1 ECPA-01 Soil D

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018


Version:       1.0
Date of this report:  22/05/2019 08:09

Study: ECPA-01D
Description:   Appendix A ECPA-01 soil D


INPUT DATA


Experimental Data

Time (days)    Total mass (µg)       Conc liq. phase (µg/mL)
0       7.62    0.0578
0       7.62    0.0568
1       7.73    0.0561
1       7.64    0.0559
3       7.32    0.0527
3       7.35    0.0517
7       6.94    0.0483
7       7.09    0.0485
14      6.44    0.0438
14      6.40    0.0435
30      5.58    0.0354
30      5.53    0.0361
58      4.56    0.0275
58      4.57    0.0271
120     3.36    0.0190
120     3.30    0.0188

Parameters

Name    Initial Value  Lower Bound    Upper Bound    Fit
M_sol   100     0       10000   False
V_sol   27.7    0       10000   False
V_add   72.3    0       10000   False
cont_OC 0.025   0       10000   False
c_LR    1       0.1     10000   False
M_0     8.042   0       10000   True
ExpFre  0.910   0.01    1.3     False
KOC_EQ  3.363   0       10000   True
f_NEQ   0.2     0       10000   True
```

k_des	0.05	0	0.5	True
DT50_EQ	90	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.03212)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	27.700	ml	System	Volume of liquid in moist soil
V_add	72.300	ml	System	Volume of liquid added
cont_OC	0.025	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	7.344	µg	System	Initial mass of pesticide
ExpFre	0.910	-	Sorption	Freundlich exponent 1/N
KOC_EQ	8.983	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.582	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.050	1/d	Sorption	Desorption rate coefficient
DT50_EQ	79.460	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	4.995
Weighted ME (Chi²)	2.802
Coeff. of Det. (R²)	0.997
Model efficiency	0.997
Abs. deviation	3.531
Quadr. deviation	0.973
SRMSE	0.056
STE	0.035

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)		0.978	0.998	
Model efficiency		0.972	0.997	
Abs. deviation	3.523	0.009		
Quadr. deviation		0.973	0.000	
SRMSE	0.040	0.015		
STE	0.036	0.013		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.620	7.344	0.27600	0.01722
0.000	7.620	7.344	0.27600	0.01722
1.000	7.730	7.281	0.44901	0.01674
1.000	7.640	7.281	0.35901	0.01713
3.000	7.320	7.158	0.16157	0.01866
3.000	7.350	7.158	0.19157	0.01851
7.000	6.940	6.928	0.01232	0.02076
7.000	7.090	6.928	0.16232	0.01989
14.000	6.440	6.563	-0.12276	0.02411
14.000	6.400	6.563	-0.16276	0.02441
30.000	5.580	5.852	-0.27201	0.03212
30.000	5.530	5.852	-0.32201	0.03270
58.000	4.560	4.850	-0.29033	0.04809
58.000	4.570	4.850	-0.28033	0.04788
120.000	3.360	3.238	0.12225	0.08858
120.000	3.300	3.238	0.06225	0.09183

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.058	0.057	0.00090	299.32592
0.000	0.057	0.057	-0.00010	309.95834
1.000	0.056	0.056	0.00049	317.74175
1.000	0.056	0.056	0.00029	320.01946
3.000	0.053	0.053	-0.00050	360.06323
3.000	0.052	0.053	-0.00150	374.12688
7.000	0.048	0.049	-0.00076	428.65287
7.000	0.049	0.049	-0.00056	425.12488
14.000	0.044	0.044	0.00028	521.25685
14.000	0.044	0.044	-0.00002	528.47140
30.000	0.035	0.036	-0.00016	797.98270
30.000	0.036	0.036	0.00054	767.33604
58.000	0.028	0.028	-0.00046	1322.31405
58.000	0.027	0.028	-0.00086	1361.63723
120.000	0.019	0.018	0.00079	2770.08310
120.000	0.019	0.018	0.00059	2829.33454

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	7.344	0.057
1.000	7.281	0.056
2.000	7.219	0.054
3.000	7.158	0.053
4.000	7.099	0.052
5.000	7.041	0.051
6.000	6.984	0.050
7.000	6.928	0.049
8.000	6.873	0.048
9.000	6.819	0.047
10.000	6.766	0.046
11.000	6.714	0.046
12.000	6.663	0.045
13.000	6.612	0.044
14.000	6.563	0.044
15.000	6.514	0.043

16.000	6.465	0.042
17.000	6.418	0.042
18.000	6.371	0.041
19.000	6.325	0.040
20.000	6.279	0.040
21.000	6.234	0.039
22.000	6.190	0.039
23.000	6.146	0.038
24.000	6.102	0.038
25.000	6.060	0.038
26.000	6.017	0.037
27.000	5.975	0.037
28.000	5.934	0.036
29.000	5.893	0.036
30.000	5.852	0.036
31.000	5.812	0.035
32.000	5.772	0.035
33.000	5.733	0.034
34.000	5.694	0.034
35.000	5.655	0.034
36.000	5.617	0.034
37.000	5.579	0.033
38.000	5.541	0.033
39.000	5.504	0.033
40.000	5.467	0.032
41.000	5.430	0.032
42.000	5.394	0.032
43.000	5.358	0.031
44.000	5.322	0.031
45.000	5.286	0.031
46.000	5.251	0.031
47.000	5.216	0.030
48.000	5.182	0.030
49.000	5.148	0.030
50.000	5.113	0.030
51.000	5.080	0.029
52.000	5.046	0.029
53.000	5.013	0.029
54.000	4.980	0.029
55.000	4.947	0.029
56.000	4.915	0.028
57.000	4.882	0.028
58.000	4.850	0.028
59.000	4.818	0.028
60.000	4.787	0.028
61.000	4.755	0.027
62.000	4.724	0.027
63.000	4.693	0.027
64.000	4.663	0.027
65.000	4.632	0.027
66.000	4.602	0.026
67.000	4.572	0.026
68.000	4.542	0.026
69.000	4.512	0.026
70.000	4.483	0.026
71.000	4.454	0.025

72.000	4.425	0.025
73.000	4.396	0.025
74.000	4.367	0.025
75.000	4.339	0.025
76.000	4.310	0.025
77.000	4.282	0.024
78.000	4.255	0.024
79.000	4.227	0.024
80.000	4.199	0.024
81.000	4.172	0.024
82.000	4.145	0.024
83.000	4.118	0.023
84.000	4.091	0.023
85.000	4.065	0.023
86.000	4.038	0.023
87.000	4.012	0.023
88.000	3.986	0.023
89.000	3.960	0.022
90.000	3.934	0.022
91.000	3.909	0.022
92.000	3.884	0.022
93.000	3.858	0.022
94.000	3.833	0.022
95.000	3.809	0.022
96.000	3.784	0.021
97.000	3.759	0.021
98.000	3.735	0.021
99.000	3.711	0.021
100.000	3.687	0.021
101.000	3.663	0.021
102.000	3.639	0.021
103.000	3.616	0.020
104.000	3.592	0.020
105.000	3.569	0.020
106.000	3.546	0.020
107.000	3.523	0.020
108.000	3.500	0.020
109.000	3.477	0.020
110.000	3.455	0.019
111.000	3.432	0.019
112.000	3.410	0.019
113.000	3.388	0.019
114.000	3.366	0.019
115.000	3.344	0.019
116.000	3.323	0.019
117.000	3.301	0.019
118.000	3.280	0.018
119.000	3.259	0.018
120.000	3.238	0.018

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to $(1/\text{observation})^2$.

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.2 ECPA-01 Soil E

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 22/05/2019 14:08

Study: ECPA-01E
Description: Appendix A ECPA-01 soil E

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	7.68	0.0600
0	7.67	0.0585
1	7.70	0.0580
1	7.66	0.0580
3	7.32	0.0536
3	7.34	0.0535
7	6.99	0.0507
7	6.99	0.0505
14	6.38	0.0454
14	6.38	0.0455
30	5.41	0.0364
30	5.43	0.0362
58	4.01	0.0255
58	4.03	0.0259
120	2.43	0.0147
120	2.48	0.0147

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	38.2	0	10000	False
V_add	61.8	0	10000	False
cont_OC	0.040	0	10000	False
c_LR	1	0.1	10000	False
M_0	8.042	0	10000	True
ExpFre	0.900	0.01	1.3	False
KOC_EQ	8.125	0	10000	True

f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	134	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.01530)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	38.200	ml	System	Volume of liquid in moist soil
V_add	61.800	ml	System	Volume of liquid added
cont_OC	0.040	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	7.510	µg	System	Initial mass of pesticide
ExpFre	0.900	-	Sorption	Freundlich exponent 1/N
KOC_EQ	5.317	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.493	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.044	1/d	Sorption	Desorption rate coefficient
DT50_EQ	60.790	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	2.968
Weighted ME (Chi²)	1.927
Coeff. of Det. (R²)	0.999
Model efficiency	0.999
Abs. deviation	1.893
Quadr. deviation	0.319
SRMSE	0.033
STE	0.020

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)	0.996	0.997		
Model efficiency	0.994	0.997		
Abs. deviation	1.884	0.009		
Quadr. deviation	0.319	0.000		
SRMSE	0.024	0.018		
STE	0.020	0.014		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.680	7.510	0.17028	0.01695
0.000	7.670	7.510	0.16028	0.01700
1.000	7.700	7.425	0.27505	0.01687
1.000	7.660	7.425	0.23505	0.01704
3.000	7.320	7.260	0.05966	0.01866
3.000	7.340	7.260	0.07966	0.01856
7.000	6.990	6.950	0.04029	0.02047
7.000	6.990	6.950	0.04029	0.02047
14.000	6.380	6.455	-0.07513	0.02457
14.000	6.380	6.455	-0.07513	0.02457
30.000	5.410	5.504	-0.09379	0.03417
30.000	5.430	5.504	-0.07379	0.03392
58.000	4.010	4.231	-0.22142	0.06219
58.000	4.030	4.231	-0.20142	0.06157
120.000	2.430	2.414	0.01628	0.16935
120.000	2.480	2.414	0.06628	0.16259

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.060	0.059	0.00144	277.77778
0.000	0.059	0.059	-0.00006	292.20542
1.000	0.058	0.057	0.00063	297.26516
1.000	0.058	0.057	0.00063	297.26516
3.000	0.054	0.055	-0.00153	348.07307
3.000	0.054	0.055	-0.00163	349.37549
7.000	0.051	0.051	-0.00042	389.03089
7.000	0.051	0.051	-0.00062	392.11842
14.000	0.045	0.045	0.00007	485.16369
14.000	0.046	0.045	0.00017	483.03345
30.000	0.036	0.036	0.00040	754.73977
30.000	0.036	0.036	0.00020	763.10247
58.000	0.026	0.026	-0.00064	1537.87005
58.000	0.026	0.026	-0.00024	1490.73508
120.000	0.015	0.014	0.00036	4627.70142
120.000	0.015	0.014	0.00036	4627.70142

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	7.510	0.059
1.000	7.425	0.057
2.000	7.342	0.056
3.000	7.260	0.055
4.000	7.180	0.054
5.000	7.102	0.053
6.000	7.025	0.052
7.000	6.949	0.051
8.000	6.875	0.050
9.000	6.802	0.049
10.000	6.730	0.048
11.000	6.660	0.048
12.000	6.590	0.047
13.000	6.522	0.046
14.000	6.455	0.045

15.000	6.389	0.045
16.000	6.323	0.044
17.000	6.259	0.043
18.000	6.196	0.043
19.000	6.134	0.042
20.000	6.073	0.041
21.000	6.012	0.041
22.000	5.953	0.040
23.000	5.894	0.040
24.000	5.836	0.039
25.000	5.779	0.038
26.000	5.722	0.038
27.000	5.667	0.037
28.000	5.612	0.037
29.000	5.557	0.036
30.000	5.504	0.036
31.000	5.451	0.036
32.000	5.399	0.035
33.000	5.347	0.035
34.000	5.296	0.034
35.000	5.246	0.034
36.000	5.196	0.033
37.000	5.147	0.033
38.000	5.098	0.033
39.000	5.050	0.032
40.000	5.003	0.032
41.000	4.956	0.031
42.000	4.909	0.031
43.000	4.864	0.031
44.000	4.818	0.030
45.000	4.773	0.030
46.000	4.729	0.030
47.000	4.685	0.029
48.000	4.642	0.029
49.000	4.599	0.029
50.000	4.556	0.028
51.000	4.514	0.028
52.000	4.472	0.028
53.000	4.431	0.028
54.000	4.390	0.027
55.000	4.350	0.027
56.000	4.310	0.027
57.000	4.271	0.026
58.000	4.231	0.026
59.000	4.193	0.026
60.000	4.154	0.026
61.000	4.116	0.025
62.000	4.079	0.025
63.000	4.042	0.025
64.000	4.005	0.025
65.000	3.968	0.024
66.000	3.932	0.024
67.000	3.896	0.024
68.000	3.861	0.024
69.000	3.826	0.023
70.000	3.791	0.023

71.000	3.757	0.023
72.000	3.723	0.023
73.000	3.689	0.022
74.000	3.656	0.022
75.000	3.623	0.022
76.000	3.590	0.022
77.000	3.557	0.022
78.000	3.525	0.021
79.000	3.493	0.021
80.000	3.462	0.021
81.000	3.431	0.021
82.000	3.400	0.021
83.000	3.369	0.020
84.000	3.339	0.020
85.000	3.308	0.020
86.000	3.279	0.020
87.000	3.249	0.020
88.000	3.220	0.019
89.000	3.191	0.019
90.000	3.162	0.019
91.000	3.134	0.019
92.000	3.106	0.019
93.000	3.078	0.019
94.000	3.050	0.018
95.000	3.023	0.018
96.000	2.995	0.018
97.000	2.969	0.018
98.000	2.942	0.018
99.000	2.916	0.017
100.000	2.889	0.017
101.000	2.863	0.017
102.000	2.838	0.017
103.000	2.812	0.017
104.000	2.787	0.017
105.000	2.762	0.017
106.000	2.737	0.016
107.000	2.713	0.016
108.000	2.689	0.016
109.000	2.664	0.016
110.000	2.641	0.016
111.000	2.617	0.016
112.000	2.594	0.015
113.000	2.570	0.015
114.000	2.547	0.015
115.000	2.525	0.015
116.000	2.502	0.015
117.000	2.480	0.015
118.000	2.457	0.015
119.000	2.435	0.014
120.000	2.414	0.014

The objective function is based on weighted least squares of observed data and by model predicted data.

The weight for each data point is equal to (1/observation)².

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.3 ECPA-01 Soil F

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 22/05/2019 14:31

Study: ECPA-01F
Description: Appendix A ECPA-01 soil F

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	7.44	0.0494
0	7.51	0.0495
1	7.21	0.0482
1	7.33	0.0490
3	7.20	0.0453
3	7.26	0.0457
7	7.16	0.0434
7	6.98	0.0425
14	6.39	0.0395
14	6.72	0.0399
30	6.03	0.0352
30	6.01	0.0355
58	5.43	0.0293
58	5.58	0.0299
120	4.64	0.0229
120	4.66	0.0231

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	42.0	0	10000	False
V_add	58.1	0	10000	False
cont_OC	0.026	0	10000	False
c_LR	1	0.1	10000	False
M_0	8.042	0	10000	True
ExpFre	0.900	0.01	1.3	False

KOC_EQ	8.125	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	64	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.02153)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	42.000	ml	System	Volume of liquid in moist soil
V_add	58.100	ml	System	Volume of liquid added
cont_OC	0.026	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	7.191	µg	System	Initial mass of pesticide
ExpFre	0.900	-	Sorption	Freundlich exponent 1/N
KOC_EQ	13.384	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.512	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.049	1/d	Sorption	Desorption rate coefficient
DT50_EQ	142.775	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	3.854
Weighted ME (Chi²)	2.164
Coeff. of Det. (R²)	0.998
Model efficiency	0.998
Abs. deviation	2.958
Quadr. deviation	0.713
SRMSE	0.046
STE	0.028

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)	0.951		0.995	
Model efficiency	0.950		0.995	
Abs. deviation	2.950		0.008	
Quadr. deviation	0.713		0.000	
SRMSE	0.033	0.016		
STE	0.028	0.013		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.440	7.191	0.24917	0.01807
0.000	7.510	7.191	0.31917	0.01773
1.000	7.210	7.156	0.05360	0.01924
1.000	7.330	7.156	0.17360	0.01861
3.000	7.200	7.089	0.11109	0.01929
3.000	7.260	7.089	0.17109	0.01897
7.000	7.160	6.960	0.20007	0.01951
7.000	6.980	6.960	0.02007	0.02053
14.000	6.390	6.751	-0.36068	0.02449
14.000	6.720	6.751	-0.03068	0.02214
30.000	6.030	6.324	-0.29395	0.02750
30.000	6.010	6.324	-0.31395	0.02769
58.000	5.430	5.677	-0.24714	0.03392
58.000	5.580	5.677	-0.09714	0.03212
120.000	4.640	4.496	0.14415	0.04645
120.000	4.660	4.496	0.16415	0.04605

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.049	0.049	0.00053	409.77561
0.000	0.050	0.049	0.00063	408.12162
1.000	0.048	0.048	0.00020	430.43336
1.000	0.049	0.048	0.00100	416.49313
3.000	0.045	0.046	-0.00109	487.30806
3.000	0.046	0.046	-0.00069	478.81484
7.000	0.043	0.044	-0.00022	530.90955
7.000	0.043	0.044	-0.00112	553.63322
14.000	0.040	0.040	-0.00040	640.92293
14.000	0.040	0.040	0.00000	628.13676
30.000	0.035	0.035	0.00059	807.07645
30.000	0.036	0.035	0.00089	793.49335
58.000	0.029	0.030	-0.00037	1164.83593
58.000	0.030	0.030	0.00023	1118.55572
120.000	0.023	0.023	-0.00011	1906.90490
120.000	0.023	0.023	0.00009	1874.02785

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	7.191	0.049
1.000	7.156	0.048
2.000	7.122	0.047
3.000	7.089	0.046
4.000	7.056	0.046
5.000	7.023	0.045
6.000	6.991	0.044
7.000	6.960	0.044
8.000	6.929	0.043
9.000	6.898	0.042
10.000	6.868	0.042
11.000	6.838	0.041
12.000	6.809	0.041
13.000	6.779	0.040

14.000	6.751	0.040
15.000	6.722	0.039
16.000	6.694	0.039
17.000	6.666	0.039
18.000	6.638	0.038
19.000	6.611	0.038
20.000	6.584	0.038
21.000	6.557	0.037
22.000	6.530	0.037
23.000	6.503	0.037
24.000	6.477	0.036
25.000	6.451	0.036
26.000	6.425	0.036
27.000	6.400	0.035
28.000	6.374	0.035
29.000	6.349	0.035
30.000	6.324	0.035
31.000	6.299	0.034
32.000	6.274	0.034
33.000	6.250	0.034
34.000	6.225	0.034
35.000	6.201	0.033
36.000	6.177	0.033
37.000	6.153	0.033
38.000	6.129	0.033
39.000	6.105	0.033
40.000	6.082	0.032
41.000	6.058	0.032
42.000	6.035	0.032
43.000	6.012	0.032
44.000	5.989	0.032
45.000	5.966	0.032
46.000	5.943	0.031
47.000	5.920	0.031
48.000	5.897	0.031
49.000	5.875	0.031
50.000	5.853	0.031
51.000	5.830	0.031
52.000	5.808	0.031
53.000	5.786	0.030
54.000	5.764	0.030
55.000	5.742	0.030
56.000	5.720	0.030
57.000	5.699	0.030
58.000	5.677	0.030
59.000	5.656	0.030
60.000	5.634	0.029
61.000	5.613	0.029
62.000	5.592	0.029
63.000	5.570	0.029
64.000	5.549	0.029
65.000	5.528	0.029
66.000	5.508	0.029
67.000	5.487	0.029
68.000	5.466	0.028
69.000	5.446	0.028

70.000	5.425	0.028
71.000	5.405	0.028
72.000	5.384	0.028
73.000	5.364	0.028
74.000	5.344	0.028
75.000	5.324	0.028
76.000	5.304	0.027
77.000	5.284	0.027
78.000	5.264	0.027
79.000	5.244	0.027
80.000	5.224	0.027
81.000	5.205	0.027
82.000	5.185	0.027
83.000	5.166	0.027
84.000	5.146	0.027
85.000	5.127	0.026
86.000	5.108	0.026
87.000	5.089	0.026
88.000	5.070	0.026
89.000	5.051	0.026
90.000	5.032	0.026
91.000	5.013	0.026
92.000	4.994	0.026
93.000	4.975	0.026
94.000	4.957	0.026
95.000	4.938	0.025
96.000	4.919	0.025
97.000	4.901	0.025
98.000	4.883	0.025
99.000	4.864	0.025
100.000	4.846	0.025
101.000	4.828	0.025
102.000	4.810	0.025
103.000	4.792	0.025
104.000	4.774	0.025
105.000	4.756	0.024
106.000	4.738	0.024
107.000	4.720	0.024
108.000	4.703	0.024
109.000	4.685	0.024
110.000	4.668	0.024
111.000	4.650	0.024
112.000	4.633	0.024
113.000	4.615	0.024
114.000	4.598	0.024
115.000	4.581	0.023
116.000	4.564	0.023
117.000	4.547	0.023
118.000	4.530	0.023
119.000	4.513	0.023
120.000	4.496	0.023

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to (1/observation)².

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.4 ECPA-01 Soil G

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 22/05/2019 14:50

Study: ECPA-01G
Description: Appendix A ECPA-01 soil G

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	7.38	0.0417
0	7.37	0.0419
1	7.36	0.0401
1	7.29	0.0399
3	6.96	0.0360
3	6.91	0.0361
7	6.76	0.0341
7	6.74	0.0339
14	6.35	0.0302
14	6.28	0.0305
30	5.40	0.0263
30	5.39	0.0257
58	4.67	0.0209
58	3.85	0.0212
120	3.82	0.0153
120	3.85	0.0154

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	30.3	0	10000	False
V_add	69.8	0	10000	False
cont_OC	0.038	0	10000	False
c_LR	1	0.1	10000	False

M_0	8.042	0	10000	True
ExpFre	0.940	0.01	1.3	False
KOC_EQ	4.196	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	212	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.12874)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	30.300	ml	System	Volume of liquid in moist soil
V_add	69.800	ml	System	Volume of liquid added
cont_OC	0.038	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	6.911	µg	System	Initial mass of pesticide
ExpFre	0.940	-	Sorption	Freundlich exponent 1/N
KOC_EQ	14.968	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.442	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.074	1/d	Sorption	Desorption rate coefficient
DT50_EQ	92.572	d	Sorption	Transformation half-life (20°C)

EVALUTATION

Complete Data Set	
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	7.962
Weighted ME (Chi²)	4.958
Coeff. of Det. (R²)	0.992
Model efficiency	0.992
Abs. deviation	5.312
Quadr. deviation	2.629
SRMSE	0.095
STE	0.055

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)		0.913	0.994	
Model efficiency		0.902	0.994	
Abs. deviation	5.304	0.008		
Quadr. deviation		2.629	0.000	
SRMSE	0.067	0.023		
STE	0.055	0.017		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.380	6.910	0.46951	0.01836
0.000	7.370	6.910	0.45951	0.01841
1.000	7.360	6.860	0.50050	0.01846
1.000	7.290	6.860	0.43050	0.01882
3.000	6.960	6.762	0.19815	0.02064
3.000	6.910	6.762	0.14815	0.02094
7.000	6.760	6.580	0.18008	0.02188
7.000	6.740	6.580	0.16008	0.02201
14.000	6.350	6.294	0.05648	0.02480
14.000	6.280	6.294	-0.01352	0.02536
30.000	5.400	5.727	-0.32668	0.03429
30.000	5.390	5.727	-0.33668	0.03442
58.000	4.670	4.887	-0.21662	0.04585
58.000	3.850	4.887	-1.03662	0.06747
120.000	3.820	3.450	0.37030	0.06853
120.000	3.850	3.450	0.40030	0.06747

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.042	0.041	0.00081	575.07950
0.000	0.042	0.041	0.00101	569.60259
1.000	0.040	0.040	0.00041	621.88668
1.000	0.040	0.040	0.00021	628.13676
3.000	0.036	0.038	-0.00158	771.60494
3.000	0.036	0.038	-0.00148	767.33604
7.000	0.034	0.034	-0.00015	859.98572
7.000	0.034	0.034	-0.00035	870.16298
14.000	0.030	0.030	-0.00016	1096.44314
14.000	0.031	0.030	0.00014	1074.97984
30.000	0.026	0.026	0.00060	1445.73436
30.000	0.026	0.026	0.00000	1514.02746
58.000	0.021	0.021	-0.00049	2289.32488
58.000	0.021	0.021	-0.00019	2224.99110
120.000	0.015	0.015	0.00039	4271.86125
120.000	0.015	0.015	0.00049	4216.56266

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	6.910	0.041
1.000	6.860	0.040
2.000	6.810	0.039
3.000	6.762	0.038
4.000	6.715	0.037
5.000	6.669	0.036
6.000	6.624	0.035
7.000	6.580	0.034
8.000	6.537	0.034
9.000	6.494	0.033
10.000	6.453	0.032
11.000	6.412	0.032

12.000	6.372	0.031
13.000	6.332	0.031
14.000	6.293	0.030
15.000	6.255	0.030
16.000	6.217	0.030
17.000	6.180	0.029
18.000	6.143	0.029
19.000	6.106	0.028
20.000	6.070	0.028
21.000	6.034	0.028
22.000	5.999	0.028
23.000	5.964	0.027
24.000	5.929	0.027
25.000	5.894	0.027
26.000	5.860	0.027
27.000	5.826	0.026
28.000	5.793	0.026
29.000	5.760	0.026
30.000	5.727	0.026
31.000	5.694	0.025
32.000	5.661	0.025
33.000	5.629	0.025
34.000	5.597	0.025
35.000	5.565	0.025
36.000	5.533	0.025
37.000	5.502	0.024
38.000	5.471	0.024
39.000	5.440	0.024
40.000	5.409	0.024
41.000	5.379	0.024
42.000	5.348	0.024
43.000	5.318	0.023
44.000	5.288	0.023
45.000	5.258	0.023
46.000	5.229	0.023
47.000	5.199	0.023
48.000	5.170	0.023
49.000	5.141	0.023
50.000	5.112	0.022
51.000	5.083	0.022
52.000	5.055	0.022
53.000	5.026	0.022
54.000	4.998	0.022
55.000	4.970	0.022
56.000	4.942	0.022
57.000	4.914	0.022
58.000	4.887	0.021
59.000	4.859	0.021
60.000	4.832	0.021
61.000	4.805	0.021
62.000	4.778	0.021
63.000	4.751	0.021
64.000	4.724	0.021
65.000	4.698	0.021
66.000	4.672	0.020
67.000	4.645	0.020

68.000	4.619	0.020
69.000	4.593	0.020
70.000	4.568	0.020
71.000	4.542	0.020
72.000	4.517	0.020
73.000	4.491	0.020
74.000	4.466	0.019
75.000	4.441	0.019
76.000	4.416	0.019
77.000	4.392	0.019
78.000	4.367	0.019
79.000	4.342	0.019
80.000	4.318	0.019
81.000	4.294	0.019
82.000	4.270	0.019
83.000	4.246	0.018
84.000	4.222	0.018
85.000	4.199	0.018
86.000	4.175	0.018
87.000	4.152	0.018
88.000	4.128	0.018
89.000	4.105	0.018
90.000	4.082	0.018
91.000	4.059	0.018
92.000	4.037	0.018
93.000	4.014	0.017
94.000	3.992	0.017
95.000	3.969	0.017
96.000	3.947	0.017
97.000	3.925	0.017
98.000	3.903	0.017
99.000	3.881	0.017
100.000	3.859	0.017
101.000	3.838	0.017
102.000	3.816	0.017
103.000	3.795	0.016
104.000	3.774	0.016
105.000	3.753	0.016
106.000	3.732	0.016
107.000	3.711	0.016
108.000	3.690	0.016
109.000	3.669	0.016
110.000	3.649	0.016
111.000	3.628	0.016
112.000	3.608	0.016
113.000	3.588	0.016
114.000	3.568	0.015
115.000	3.548	0.015
116.000	3.528	0.015
117.000	3.508	0.015
118.000	3.489	0.015
119.000	3.469	0.015
120.000	3.450	0.015

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to $(1/observation)^2$.

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.5 ECPA-06 Soil A

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 23/05/2019 06:58

Study: ECPA-06A
Description: Appendix B ECPA-06 soil A

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	66.08	0.0695
0	66.74	0.0703
1	67.31	0.0623
1	67.01	0.0641
3	67.56	0.0604
3	67.27	0.0597
8	64.49	0.0524
8	65.29	0.0534
14	65.04	0.0462
14	65.69	0.0462
28	56.52	0.0349
28	58.85	0.0377
58	51.21	0.0278
58	51.43	0.0291
120	41.26	0.0222
120	42.27	0.0229

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	25.1	0	10000	False
V_add	400.0	0	10000	False
cont_OC	0.013	0	10000	False

c_LR	1	0.1	10000	False
M_0	68.4	0	10000	True
ExpFre	0.895	0.01	1.3	False
KOC_EQ	600	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.004	0	1	True
DT50_EQ	162	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.01926)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	25.100	ml	System	Volume of liquid in moist soil
V_add	400.000	ml	System	Volume of liquid added
cont_OC	0.013	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	67.642	µg	System	Initial mass of pesticide
ExpFre	0.895	-	Sorption	Freundlich exponent 1/N
KOC_EQ	335.299	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.705	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.040	1/d	Sorption	Desorption rate coefficient
DT50_EQ	107.804	d	Sorption	Transformation half-life (20°C)

EVALUTATION

Complete Data Set	
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	2.665
Weighted ME (Chi²)	1.787
Coeff. of Det. (R²)	0.999
Model efficiency	0.999
Abs. deviation	16.578
Quadr. deviation	29.489
SRMSE	0.032
STE	0.017

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)		0.977	0.993	
Model efficiency		0.976	0.993	
Abs. deviation	16.561	0.018		
Quadr. deviation		29.489	0.000	
SRMSE	0.023	0.029		
STE	0.017	0.023		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	66.080	67.639	-1.55949	0.00023
0.000	66.740	67.639	-0.89949	0.00022
1.000	67.310	67.212	0.09834	0.00022
1.000	67.010	67.212	-0.20166	0.00022
3.000	67.560	66.396	1.16432	0.00022
3.000	67.270	66.396	0.87432	0.00022
8.000	64.490	64.553	-0.06350	0.00024
8.000	65.290	64.553	0.73650	0.00023
14.000	65.040	62.623	2.41737	0.00024
14.000	65.690	62.623	3.06737	0.00023
28.000	56.520	58.857	-2.33678	0.00031
28.000	58.850	58.857	-0.00678	0.00029
58.000	51.210	52.382	-1.17231	0.00038
58.000	51.430	52.382	-0.95231	0.00038
120.000	41.260	41.650	-0.38953	0.00059
120.000	42.270	41.650	0.62047	0.00056

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.070	0.067	0.00211	207.02862
0.000	0.070	0.067	0.00291	202.34354
1.000	0.062	0.065	-0.00280	257.64630
1.000	0.064	0.065	-0.00100	243.37947
3.000	0.060	0.061	-0.00053	274.11078
3.000	0.060	0.061	-0.00123	280.57653
8.000	0.052	0.053	-0.00024	364.19789
8.000	0.053	0.053	0.00076	350.68524
14.000	0.046	0.046	0.00059	468.50696
14.000	0.046	0.046	0.00059	468.50696
28.000	0.035	0.036	-0.00147	821.01132
28.000	0.038	0.036	0.00133	703.58618
58.000	0.028	0.029	-0.00107	1293.92889
58.000	0.029	0.029	0.00023	1180.90245
120.000	0.022	0.022	0.00001	2029.05608
120.000	0.023	0.022	0.00071	1906.90490

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	67.639	0.067
1.000	67.212	0.065
2.000	66.797	0.063
3.000	66.396	0.061
4.000	66.006	0.059
5.000	65.627	0.057
6.000	65.259	0.056
7.000	64.901	0.054
8.000	64.551	0.053
9.000	64.211	0.051
10.000	63.878	0.050

11.000	63.554	0.049
12.000	63.236	0.048
13.000	62.925	0.047
14.000	62.621	0.046
15.000	62.322	0.045
16.000	62.030	0.044
17.000	61.742	0.043
18.000	61.460	0.042
19.000	61.182	0.041
20.000	60.908	0.041
21.000	60.639	0.040
22.000	60.374	0.039
23.000	60.113	0.039
24.000	59.855	0.038
25.000	59.601	0.038
26.000	59.350	0.037
27.000	59.102	0.037
28.000	58.857	0.036
29.000	58.614	0.036
30.000	58.375	0.036
31.000	58.137	0.035
32.000	57.902	0.035
33.000	57.670	0.034
34.000	57.439	0.034
35.000	57.211	0.034
36.000	56.985	0.033
37.000	56.760	0.033
38.000	56.538	0.033
39.000	56.317	0.033
40.000	56.097	0.032
41.000	55.880	0.032
42.000	55.664	0.032
43.000	55.449	0.032
44.000	55.236	0.031
45.000	55.024	0.031
46.000	54.814	0.031
47.000	54.605	0.031
48.000	54.397	0.031
49.000	54.191	0.030
50.000	53.986	0.030
51.000	53.781	0.030
52.000	53.578	0.030
53.000	53.376	0.030
54.000	53.176	0.030
55.000	52.976	0.029
56.000	52.777	0.029
57.000	52.579	0.029
58.000	52.382	0.029
59.000	52.186	0.029
60.000	51.992	0.029
61.000	51.798	0.028
62.000	51.604	0.028
63.000	51.412	0.028
64.000	51.221	0.028
65.000	51.030	0.028
66.000	50.841	0.028

67.000	50.652	0.028
68.000	50.464	0.027
69.000	50.277	0.027
70.000	50.091	0.027
71.000	49.905	0.027
72.000	49.720	0.027
73.000	49.536	0.027
74.000	49.353	0.027
75.000	49.171	0.027
76.000	48.989	0.027
77.000	48.808	0.026
78.000	48.627	0.026
79.000	48.448	0.026
80.000	48.269	0.026
81.000	48.091	0.026
82.000	47.913	0.026
83.000	47.737	0.026
84.000	47.561	0.026
85.000	47.385	0.026
86.000	47.211	0.025
87.000	47.037	0.025
88.000	46.863	0.025
89.000	46.691	0.025
90.000	46.519	0.025
91.000	46.347	0.025
92.000	46.177	0.025
93.000	46.007	0.025
94.000	45.837	0.025
95.000	45.668	0.025
96.000	45.500	0.024
97.000	45.333	0.024
98.000	45.166	0.024
99.000	45.000	0.024
100.000	44.834	0.024
101.000	44.669	0.024
102.000	44.505	0.024
103.000	44.341	0.024
104.000	44.178	0.024
105.000	44.016	0.024
106.000	43.854	0.023
107.000	43.692	0.023
108.000	43.532	0.023
109.000	43.372	0.023
110.000	43.212	0.023
111.000	43.053	0.023
112.000	42.895	0.023
113.000	42.737	0.023
114.000	42.580	0.023
115.000	42.424	0.023
116.000	42.268	0.023
117.000	42.112	0.022
118.000	41.957	0.022
119.000	41.803	0.022
120.000	41.650	0.022

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to (1/observation)².

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.6 ECPA-06 Soil B

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 23/05/2019 07:48

Study: ECPA-06B
Description: Appendix B ECPA-06 soil B

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	62.54	0.0784
0	62.98	0.0802
1	61.15	0.0693
1	62.69	0.0729
3	59.19	0.0672
3	60.43	0.0661
8	59.54	0.0608
8	58.39	0.0606
14	62.10	0.0584
14	61.99	0.0586
28	51.80	0.0446
28	52.38	0.0451
58	45.46	0.0342
58	43.69	0.0314
120	34.03	0.0236
120	32.92	0.0211

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	28.6	0	10000	False
V_add	400.0	0	10000	False

cont_OC	0.011	0	10000	False
c_LR	1	0.1	10000	False
M_0	64.7	0	10000	True
ExpFre	0.920	0.01	1.3	False
KOC_EQ	600	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.004	0	1	True
DT50_EQ	128	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.04739)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	28.600	ml	System	Volume of liquid in moist soil
V_add	400.000	ml	System	Volume of liquid added
cont_OC	0.011	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	63.072	µg	System	Initial mass of pesticide
ExpFre	0.920	-	Sorption	Freundlich exponent 1/N
KOC_EQ	312.575	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.605	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.024	1/d	Sorption	Desorption rate coefficient
DT50_EQ	90.196	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	4.413
Weighted ME (Chi²)	2.920
Coeff. of Det. (R²)	0.998
Model efficiency	0.998
Abs. deviation	20.504
Quadr. deviation	61.994
SRMSE	0.051
STE	0.024

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)	0.960	0.980		
Model efficiency	0.960	0.980		
Abs. deviation	20.470	0.034		
Quadr. deviation	61.994	0.000		
SRMSE	0.036	0.048		
STE	0.023	0.039		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	62.540	63.067	-0.52740	0.00026
0.000	62.980	63.067	-0.08740	0.00025
1.000	61.150	62.588	-1.43786	0.00027
1.000	62.690	62.588	0.10214	0.00025
3.000	59.190	61.658	-2.46837	0.00029
3.000	60.430	61.658	-1.22837	0.00027
8.000	59.540	59.496	0.04423	0.00028
8.000	58.390	59.496	-1.10577	0.00029
14.000	62.100	57.145	4.95518	0.00026
14.000	61.990	57.145	4.84518	0.00026
28.000	51.800	52.484	-0.68412	0.00037
28.000	52.380	52.484	-0.10412	0.00036
58.000	45.460	44.811	0.64924	0.00048
58.000	43.690	44.811	-1.12076	0.00052
120.000	34.030	33.507	0.52302	0.00086
120.000	32.920	33.507	-0.58698	0.00092

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.078	0.074	0.00438	162.69263
0.000	0.080	0.074	0.00618	155.47167
1.000	0.069	0.072	-0.00311	208.22532
1.000	0.073	0.072	0.00049	188.16764
3.000	0.067	0.069	-0.00215	221.44274
3.000	0.066	0.069	-0.00325	228.87433
8.000	0.061	0.063	-0.00184	270.51593
8.000	0.061	0.063	-0.00204	272.30446
14.000	0.058	0.056	0.00238	293.20698
14.000	0.059	0.056	0.00258	291.20898
28.000	0.045	0.045	-0.00044	502.72477
28.000	0.045	0.045	0.00006	491.63967
58.000	0.034	0.033	0.00150	854.96392
58.000	0.031	0.033	-0.00130	1014.23993
120.000	0.024	0.022	0.00134	1795.46107
120.000	0.021	0.022	-0.00116	2246.13104

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	63.067	0.074
1.000	62.588	0.072
2.000	62.118	0.071
3.000	61.658	0.069
4.000	61.208	0.068
5.000	60.766	0.067
6.000	60.333	0.065
7.000	59.908	0.064
8.000	59.491	0.063
9.000	59.083	0.061

10.000	58.681	0.060
11.000	58.287	0.059
12.000	57.899	0.058
13.000	57.519	0.057
14.000	57.145	0.056
15.000	56.777	0.055
16.000	56.415	0.054
17.000	56.059	0.053
18.000	55.709	0.052
19.000	55.365	0.051
20.000	55.025	0.051
21.000	54.691	0.050
22.000	54.362	0.049
23.000	54.037	0.048
24.000	53.717	0.048
25.000	53.402	0.047
26.000	53.091	0.046
27.000	52.784	0.046
28.000	52.481	0.045
29.000	52.182	0.044
30.000	51.887	0.044
31.000	51.596	0.043
32.000	51.308	0.043
33.000	51.024	0.042
34.000	50.743	0.042
35.000	50.466	0.041
36.000	50.192	0.041
37.000	49.920	0.040
38.000	49.652	0.040
39.000	49.387	0.039
40.000	49.125	0.039
41.000	48.865	0.038
42.000	48.608	0.038
43.000	48.354	0.038
44.000	48.102	0.037
45.000	47.853	0.037
46.000	47.606	0.036
47.000	47.361	0.036
48.000	47.119	0.036
49.000	46.879	0.035
50.000	46.641	0.035
51.000	46.405	0.035
52.000	46.172	0.034
53.000	45.940	0.034
54.000	45.710	0.034
55.000	45.483	0.034
56.000	45.257	0.033
57.000	45.033	0.033
58.000	44.811	0.033
59.000	44.590	0.032
60.000	44.372	0.032
61.000	44.155	0.032
62.000	43.939	0.032
63.000	43.726	0.031
64.000	43.513	0.031
65.000	43.303	0.031

66.000	43.094	0.031
67.000	42.886	0.030
68.000	42.680	0.030
69.000	42.475	0.030
70.000	42.272	0.030
71.000	42.070	0.030
72.000	41.869	0.029
73.000	41.670	0.029
74.000	41.472	0.029
75.000	41.276	0.029
76.000	41.080	0.029
77.000	40.886	0.028
78.000	40.693	0.028
79.000	40.501	0.028
80.000	40.311	0.028
81.000	40.122	0.028
82.000	39.933	0.028
83.000	39.746	0.027
84.000	39.560	0.027
85.000	39.376	0.027
86.000	39.192	0.027
87.000	39.009	0.027
88.000	38.828	0.027
89.000	38.647	0.026
90.000	38.467	0.026
91.000	38.289	0.026
92.000	38.111	0.026
93.000	37.935	0.026
94.000	37.759	0.026
95.000	37.585	0.025
96.000	37.411	0.025
97.000	37.238	0.025
98.000	37.066	0.025
99.000	36.896	0.025
100.000	36.726	0.025
101.000	36.557	0.025
102.000	36.388	0.024
103.000	36.221	0.024
104.000	36.055	0.024
105.000	35.889	0.024
106.000	35.725	0.024
107.000	35.561	0.024
108.000	35.398	0.024
109.000	35.236	0.024
110.000	35.074	0.023
111.000	34.914	0.023
112.000	34.754	0.023
113.000	34.595	0.023
114.000	34.437	0.023
115.000	34.280	0.023
116.000	34.124	0.023
117.000	33.968	0.023
118.000	33.813	0.022
119.000	33.659	0.022
120.000	33.505	0.022

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to $(1/observation)^2$.

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.7 ECPA-06 Soil C

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 23/05/2019 07:56

Study: ECPA-06C
Description: Appendix B ECPA-06 soil C

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	66.26	0.0633
0	68.42	0.0654
1	68.24	0.0608
1	69.11	0.0622
3	66.00	0.0547
3	64.42	0.0551
8	64.69	0.0502
8	63.78	0.0498
14	68.64	0.0470
14	67.96	0.0468
28	60.50	0.0389
28	59.67	0.0390
58	54.04	0.0321
58	55.02	0.0313
120	47.48	0.0279
120	50.97	0.0309

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	31.6	0	10000	False

V_add	400.0	0	10000	False
cont_OC	0.015	0	10000	False
c_LR	1	0.1	10000	False
M_0	69.8	0	10000	True
ExpFre	0.974	0.01	1.3	False
KOC_EQ	600	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.004	0	1	True
DT50_EQ	128	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.04199)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	31.600	ml	System	Volume of liquid in moist soil
V_add	400.000	ml	System	Volume of liquid added
cont_OC	0.015	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	67.000	µg	System	Initial mass of pesticide
ExpFre	0.974	-	Sorption	Freundlich exponent 1/N
KOC_EQ	396.421	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.598	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.046	1/d	Sorption	Desorption rate coefficient
DT50_EQ	175.792	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	4.142
Weighted ME (Chi²)	2.882
Coeff. of Det. (R²)	0.998
Model efficiency	0.998
Abs. deviation	29.537
Quadr. deviation	76.919
SRMSE	0.050
STE	0.030

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)	0.897	0.982		
Model efficiency	0.892	0.982		
Abs. deviation	29.516	0.022		
Quadr. deviation	76.919	0.000		
SRMSE	0.035	0.034		
STE	0.030	0.029		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	66.260	66.999	-0.73883	0.00023
0.000	68.420	66.999	1.42117	0.00021
1.000	68.240	66.739	1.50146	0.00021
1.000	69.110	66.739	2.37146	0.00021
3.000	66.000	66.240	-0.23959	0.00023
3.000	64.420	66.240	-1.81959	0.00024
8.000	64.690	65.099	-0.40906	0.00024
8.000	63.780	65.099	-1.31906	0.00025
14.000	68.640	63.878	4.76182	0.00021
14.000	67.960	63.878	4.08182	0.00022
28.000	60.500	61.407	-0.90726	0.00027
28.000	59.670	61.407	-1.73726	0.00028
58.000	54.040	56.889	-2.84860	0.00034
58.000	55.020	56.889	-1.86860	0.00033
120.000	47.480	48.821	-1.34140	0.00044
120.000	50.970	48.821	2.14860	0.00038

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.063	0.063	0.00072	249.57012
0.000	0.065	0.063	0.00282	233.80000
1.000	0.061	0.061	0.00006	270.51593
1.000	0.062	0.061	0.00146	258.47541
3.000	0.055	0.057	-0.00273	334.21455
3.000	0.055	0.057	-0.00233	329.37968
8.000	0.050	0.051	-0.00070	396.81910
8.000	0.050	0.051	-0.00110	403.21930
14.000	0.047	0.045	0.00153	452.69353
14.000	0.047	0.045	0.00133	456.57097
28.000	0.039	0.039	0.00036	660.84681
28.000	0.039	0.039	0.00046	657.46220
58.000	0.032	0.033	-0.00107	970.48748
58.000	0.031	0.033	-0.00187	1020.73105
120.000	0.028	0.028	-0.00021	1284.67003
120.000	0.031	0.028	0.00279	1047.32879

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	66.999	0.063
1.000	66.739	0.061
2.000	66.486	0.059
3.000	66.240	0.057
4.000	66.000	0.056
5.000	65.766	0.055
6.000	65.538	0.053
7.000	65.316	0.052
8.000	65.098	0.051

9.000	64.884	0.050
10.000	64.675	0.049
11.000	64.470	0.048
12.000	64.269	0.047
13.000	64.071	0.046
14.000	63.877	0.045
15.000	63.686	0.045
16.000	63.497	0.044
17.000	63.311	0.043
18.000	63.128	0.043
19.000	62.947	0.042
20.000	62.769	0.042
21.000	62.592	0.041
22.000	62.418	0.041
23.000	62.245	0.040
24.000	62.075	0.040
25.000	61.905	0.040
26.000	61.738	0.039
27.000	61.572	0.039
28.000	61.407	0.039
29.000	61.244	0.038
30.000	61.082	0.038
31.000	60.921	0.038
32.000	60.762	0.037
33.000	60.603	0.037
34.000	60.445	0.037
35.000	60.289	0.037
36.000	60.133	0.036
37.000	59.979	0.036
38.000	59.825	0.036
39.000	59.672	0.036
40.000	59.520	0.036
41.000	59.368	0.035
42.000	59.217	0.035
43.000	59.067	0.035
44.000	58.918	0.035
45.000	58.770	0.035
46.000	58.621	0.035
47.000	58.474	0.035
48.000	58.327	0.034
49.000	58.181	0.034
50.000	58.035	0.034
51.000	57.890	0.034
52.000	57.746	0.034
53.000	57.602	0.034
54.000	57.458	0.034
55.000	57.315	0.034
56.000	57.172	0.033
57.000	57.030	0.033
58.000	56.889	0.033
59.000	56.747	0.033
60.000	56.607	0.033
61.000	56.466	0.033
62.000	56.326	0.033
63.000	56.187	0.033
64.000	56.048	0.033

65.000	55.909	0.032
66.000	55.771	0.032
67.000	55.633	0.032
68.000	55.496	0.032
69.000	55.359	0.032
70.000	55.222	0.032
71.000	55.086	0.032
72.000	54.950	0.032
73.000	54.814	0.032
74.000	54.679	0.032
75.000	54.544	0.032
76.000	54.410	0.031
77.000	54.276	0.031
78.000	54.142	0.031
79.000	54.008	0.031
80.000	53.875	0.031
81.000	53.743	0.031
82.000	53.610	0.031
83.000	53.478	0.031
84.000	53.347	0.031
85.000	53.215	0.031
86.000	53.084	0.031
87.000	52.954	0.031
88.000	52.823	0.030
89.000	52.693	0.030
90.000	52.564	0.030
91.000	52.434	0.030
92.000	52.305	0.030
93.000	52.177	0.030
94.000	52.048	0.030
95.000	51.920	0.030
96.000	51.793	0.030
97.000	51.665	0.030
98.000	51.538	0.030
99.000	51.411	0.030
100.000	51.285	0.030
101.000	51.159	0.029
102.000	51.033	0.029
103.000	50.908	0.029
104.000	50.782	0.029
105.000	50.658	0.029
106.000	50.533	0.029
107.000	50.409	0.029
108.000	50.285	0.029
109.000	50.161	0.029
110.000	50.038	0.029
111.000	49.915	0.029
112.000	49.792	0.029
113.000	49.670	0.029
114.000	49.548	0.029
115.000	49.426	0.028
116.000	49.304	0.028
117.000	49.183	0.028
118.000	49.062	0.028
119.000	48.942	0.028
120.000	48.821	0.028

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to (1/observation)².

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.8 ECPA-06 Soil D

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 1.0
Date of this report: 23/05/2019 08:07

Study: ECPA-06D
Description: Appendix B ECPA-06 soil D

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	64.07	0.0569
0	65.39	0.0569
1	63.97	0.0533
1	68.27	0.0546
3	62.64	0.0499
3	63.46	0.0493
8	61.61	0.0444
8	61.58	0.0438
14	62.31	0.0443
14	63.51	0.0423
28	53.55	0.0291
28	53.35	0.0301
58	46.00	0.0221
58	43.88	0.0210
120	33.06	0.0148
120	33.09	0.0149

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False

V_sol	36.9	0	10000	False
V_add	400.0	0	10000	False
cont_OC	0.018	0	10000	False
c_LR	1	0.1	10000	False
M_0	67.0	0	10000	True
ExpFre	0.908	0.01	1.3	False
KOC_EQ	600	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.004	0	1	True
DT50_EQ	115	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.03976)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	36.900	ml	System	Volume of liquid in moist soil
V_add	400.000	ml	System	Volume of liquid added
cont_OC	0.018	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	65.946	µg	System	Initial mass of pesticide
ExpFre	0.908	-	Sorption	Freundlich exponent 1/N
KOC_EQ	318.403	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.668	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.028	1/d	Sorption	Desorption rate coefficient
DT50_EQ	78.683	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	3.486
Weighted ME (Chi²)	2.890
Coeff. of Det. (R²)	0.998
Model efficiency	0.998
Abs. deviation	20.380
Quadr. deviation	51.301
SRMSE	0.045
STE	0.023

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	16	16		
Coeff. of Det. (R²)	0.974	0.986		
Model efficiency	0.974	0.986		
Abs. deviation	20.360	0.021		
Quadr. deviation	51.301	0.000		
SRMSE	0.032	0.044		

STE 0.023 0.033

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	64.070	65.941	-1.87092	0.00024
0.000	65.390	65.941	-0.55092	0.00023
1.000	63.970	65.368	-1.39761	0.00024
1.000	68.270	65.368	2.90239	0.00021
3.000	62.640	64.264	-1.62443	0.00025
3.000	63.460	64.264	-0.80443	0.00025
8.000	61.610	61.736	-0.12600	0.00026
8.000	61.580	61.736	-0.15600	0.00026
14.000	62.310	59.046	3.26396	0.00026
14.000	63.510	59.046	4.46396	0.00025
28.000	53.550	53.844	-0.29406	0.00035
28.000	53.350	53.844	-0.49406	0.00035
58.000	46.000	45.484	0.51571	0.00047
58.000	43.880	45.484	-1.60429	0.00052
120.000	33.060	33.221	-0.16058	0.00091
120.000	33.090	33.221	-0.13058	0.00091

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.057	0.056	0.00122	308.86981
0.000	0.057	0.056	0.00122	308.86981
1.000	0.053	0.054	-0.00085	352.00237
1.000	0.055	0.054	0.00045	335.43990
3.000	0.050	0.051	-0.00140	401.60481
3.000	0.049	0.051	-0.00200	411.43967
8.000	0.044	0.045	-0.00082	507.26402
8.000	0.044	0.045	-0.00142	521.25685
14.000	0.044	0.039	0.00481	509.55674
14.000	0.042	0.039	0.00281	558.88090
28.000	0.029	0.031	-0.00154	1180.90245
28.000	0.030	0.031	-0.00054	1103.74058
58.000	0.022	0.022	0.00032	2047.46013
58.000	0.021	0.022	-0.00078	2267.57370
120.000	0.015	0.015	0.00016	4565.37619
120.000	0.015	0.015	0.00026	4504.30161

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	65.941	0.056
1.000	65.368	0.054
2.000	64.809	0.053
3.000	64.264	0.051
4.000	63.733	0.050
5.000	63.215	0.049
6.000	62.709	0.047
7.000	62.215	0.046

8.000	61.732	0.045
9.000	61.260	0.044
10.000	60.798	0.043
11.000	60.346	0.042
12.000	59.904	0.041
13.000	59.471	0.040
14.000	59.046	0.039
15.000	58.630	0.039
16.000	58.222	0.038
17.000	57.821	0.037
18.000	57.428	0.036
19.000	57.042	0.036
20.000	56.663	0.035
21.000	56.290	0.034
22.000	55.924	0.034
23.000	55.563	0.033
24.000	55.209	0.033
25.000	54.860	0.032
26.000	54.516	0.032
27.000	54.178	0.031
28.000	53.844	0.031
29.000	53.515	0.030
30.000	53.191	0.030
31.000	52.872	0.029
32.000	52.556	0.029
33.000	52.245	0.028
34.000	51.938	0.028
35.000	51.635	0.028
36.000	51.335	0.027
37.000	51.039	0.027
38.000	50.746	0.027
39.000	50.457	0.026
40.000	50.171	0.026
41.000	49.889	0.026
42.000	49.609	0.025
43.000	49.332	0.025
44.000	49.058	0.025
45.000	48.787	0.025
46.000	48.519	0.024
47.000	48.253	0.024
48.000	47.990	0.024
49.000	47.729	0.024
50.000	47.471	0.023
51.000	47.215	0.023
52.000	46.962	0.023
53.000	46.710	0.023
54.000	46.461	0.023
55.000	46.214	0.022
56.000	45.969	0.022
57.000	45.725	0.022
58.000	45.484	0.022
59.000	45.245	0.022
60.000	45.008	0.021
61.000	44.772	0.021
62.000	44.538	0.021
63.000	44.306	0.021

64.000	44.076	0.021
65.000	43.847	0.021
66.000	43.620	0.020
67.000	43.395	0.020
68.000	43.171	0.020
69.000	42.949	0.020
70.000	42.728	0.020
71.000	42.509	0.020
72.000	42.291	0.020
73.000	42.075	0.019
74.000	41.860	0.019
75.000	41.646	0.019
76.000	41.434	0.019
77.000	41.223	0.019
78.000	41.014	0.019
79.000	40.806	0.019
80.000	40.599	0.019
81.000	40.393	0.018
82.000	40.189	0.018
83.000	39.986	0.018
84.000	39.784	0.018
85.000	39.583	0.018
86.000	39.383	0.018
87.000	39.185	0.018
88.000	38.988	0.018
89.000	38.792	0.017
90.000	38.597	0.017
91.000	38.403	0.017
92.000	38.210	0.017
93.000	38.018	0.017
94.000	37.828	0.017
95.000	37.638	0.017
96.000	37.450	0.017
97.000	37.262	0.017
98.000	37.076	0.017
99.000	36.891	0.016
100.000	36.706	0.016
101.000	36.523	0.016
102.000	36.341	0.016
103.000	36.159	0.016
104.000	35.979	0.016
105.000	35.800	0.016
106.000	35.621	0.016
107.000	35.444	0.016
108.000	35.267	0.016
109.000	35.091	0.016
110.000	34.917	0.015
111.000	34.743	0.015
112.000	34.570	0.015
113.000	34.398	0.015
114.000	34.227	0.015
115.000	34.057	0.015
116.000	33.888	0.015
117.000	33.719	0.015
118.000	33.552	0.015
119.000	33.385	0.015

120.000 33.219 0.015

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to (1/observation)².

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.9 ECPA-07 Soil A

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 18/02/2019
Date of this report: 10/05/2019 10:01

Study: ECPA-07A
Description: Appendix C in EFSA PPR Panel 2018

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	48.21	0.0887
0	48.21	0.0887
0	48.64	0.0897
1	47.68	0.0793
1	47.54	0.0789
3	44.25	0.0769
3	44.46	0.0771
7	42.17	0.0677
7	42.64	0.0683
14	38.27	0.0559
14	38.60	0.0554
21	35.72	0.0487
21	35.95	0.0485
30	31.44	0.0411
30	31.89	0.0411
59	25.05	0.0277
59	25.03	0.0281
120	18.98	0.0177
120	18.28	0.0178

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	23.2	0	10000	False
V_add	376.8	0	10000	False
cont_OC	0.012	0	10000	False
c_LR	1	0.1	10000	False
M_0	50.2	0	10000	True
ExpFre	0.845	0.01	1.3	False
KOC_EQ	98.9	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	171.4	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.05947)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	23.200	ml	System	Volume of liquid in moist soil
V_add	376.800	ml	System	Volume of liquid added
cont_OC	0.012	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	45.580	µg	System	Initial mass of pesticide
ExpFre	0.845	-	Sorption	Freundlich exponent 1/N
KOC_EQ	74.243	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.754	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.033	1/d	Sorption	Desorption rate coefficient
DT50_EQ	55.108	d	Sorption	Transformation half-life (20°C)

EVALUTATION

	Complete Data Set
No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	5.775
Weighted ME (Chi²)	3.467
Coeff. of Det. (R²)	0.996
Model efficiency	0.996
Abs. deviation	28.241
Quadr. deviation	59.424
SRMSE	0.067
STE	0.040

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R²)	0.975	0.994
Model efficiency	0.967	0.994

Abs. deviation	28.216	0.026
Quadr. deviation	59.424	0.000
SRMSE	0.047	0.033
STE	0.040	0.023

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210	45.576	2.63356	0.00043
0.000	48.210	45.576	2.63356	0.00043
0.000	48.640	45.572	3.06754	0.00042
1.000	47.680	45.013	2.66748	0.00044
1.000	47.540	45.013	2.52748	0.00044
3.000	44.250	43.941	0.30867	0.00051
3.000	44.460	43.941	0.51867	0.00051
7.000	42.170	41.979	0.19059	0.00056
7.000	42.640	41.979	0.66059	0.00055
14.000	38.270	39.032	-0.76151	0.00068
14.000	38.600	39.032	-0.43151	0.00067
21.000	35.720	36.541	-0.82147	0.00078
21.000	35.950	36.541	-0.59147	0.00077
30.000	31.440	33.816	-2.37615	0.00101
30.000	31.890	33.816	-1.92615	0.00098
59.000	25.050	27.092	-2.04158	0.00159
59.000	25.030	27.092	-2.06158	0.00160
120.000	18.980	17.632	1.34803	0.00278
120.000	18.280	17.632	0.64803	0.00299

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.089	0.086	0.00275	127.10211
0.000	0.089	0.086	0.00275	127.10211
0.000	0.090	0.086	0.00377	124.28397
1.000	0.079	0.083	-0.00377	159.02069
1.000	0.079	0.083	-0.00417	160.63715
3.000	0.077	0.078	-0.00088	169.10145
3.000	0.077	0.078	-0.00068	168.22527
7.000	0.068	0.069	-0.00101	218.18388
7.000	0.068	0.069	-0.00041	214.36733
14.000	0.056	0.057	-0.00083	320.01946
14.000	0.055	0.057	-0.00133	325.82205
21.000	0.049	0.048	0.00045	421.64026
21.000	0.049	0.048	0.00025	425.12488
30.000	0.041	0.041	0.00041	591.99271
30.000	0.041	0.041	0.00041	591.99271
59.000	0.028	0.028	-0.00047	1303.28820
59.000	0.028	0.028	-0.00007	1266.44799
120.000	0.018	0.017	0.00052	3191.93080
120.000	0.018	0.017	0.00062	3156.16715

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	45.576	0.086
1.000	45.013	0.083
2.000	44.467	0.080
3.000	43.938	0.078
4.000	43.425	0.075
5.000	42.928	0.073
6.000	42.445	0.071
7.000	41.976	0.069
8.000	41.521	0.067
9.000	41.077	0.065
10.000	40.646	0.063
11.000	40.226	0.061
12.000	39.817	0.060
13.000	39.418	0.058
14.000	39.029	0.057
15.000	38.649	0.055
16.000	38.278	0.054
17.000	37.915	0.053
18.000	37.561	0.052
19.000	37.214	0.050
20.000	36.874	0.049
21.000	36.541	0.048
22.000	36.216	0.047
23.000	35.896	0.046
24.000	35.583	0.045
25.000	35.275	0.045
26.000	34.973	0.044
27.000	34.676	0.043
28.000	34.385	0.042
29.000	34.098	0.041
30.000	33.816	0.041
31.000	33.539	0.040
32.000	33.266	0.039
33.000	32.997	0.039
34.000	32.732	0.038
35.000	32.471	0.038
36.000	32.214	0.037
37.000	31.961	0.036
38.000	31.710	0.036
39.000	31.464	0.035
40.000	31.220	0.035
41.000	30.980	0.035
42.000	30.742	0.034
43.000	30.508	0.034
44.000	30.276	0.033
45.000	30.047	0.033
46.000	29.821	0.032
47.000	29.598	0.032
48.000	29.377	0.032
49.000	29.158	0.031
50.000	28.942	0.031
51.000	28.728	0.031
52.000	28.516	0.030
53.000	28.306	0.030
54.000	28.099	0.030

55.000	27.893	0.029
56.000	27.690	0.029
57.000	27.489	0.029
58.000	27.289	0.028
59.000	27.092	0.028
60.000	26.896	0.028
61.000	26.702	0.028
62.000	26.510	0.027
63.000	26.319	0.027
64.000	26.131	0.027
65.000	25.944	0.027
66.000	25.758	0.026
67.000	25.574	0.026
68.000	25.392	0.026
69.000	25.212	0.026
70.000	25.032	0.025
71.000	24.855	0.025
72.000	24.679	0.025
73.000	24.504	0.025
74.000	24.331	0.025
75.000	24.159	0.024
76.000	23.988	0.024
77.000	23.819	0.024
78.000	23.651	0.024
79.000	23.485	0.024
80.000	23.319	0.023
81.000	23.156	0.023
82.000	22.993	0.023
83.000	22.832	0.023
84.000	22.671	0.023
85.000	22.513	0.022
86.000	22.355	0.022
87.000	22.198	0.022
88.000	22.043	0.022
89.000	21.889	0.022
90.000	21.736	0.022
91.000	21.584	0.021
92.000	21.433	0.021
93.000	21.284	0.021
94.000	21.135	0.021
95.000	20.988	0.021
96.000	20.842	0.021
97.000	20.697	0.020
98.000	20.552	0.020
99.000	20.409	0.020
100.000	20.267	0.020
101.000	20.126	0.020
102.000	19.986	0.020
103.000	19.847	0.020
104.000	19.709	0.019
105.000	19.572	0.019
106.000	19.436	0.019
107.000	19.301	0.019
108.000	19.167	0.019
109.000	19.034	0.019
110.000	18.902	0.019

111.000	18.771	0.018
112.000	18.641	0.018
113.000	18.512	0.018
114.000	18.383	0.018
115.000	18.256	0.018
116.000	18.129	0.018
117.000	18.004	0.018
118.000	17.879	0.017
119.000	17.755	0.017
120.000	17.632	0.017

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to (1/observation)².

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.10 ECPA-07 Soil B

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 18/02/2019
Date of this report: 10/05/2019 10:04

Study: ECPA-07B
Description: Appendix C in EFSA PPR Panel 2018

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	48.21	0.0887
0	47.84	0.0815
0	47.81	0.0818
1	46.81	0.0714
1	48.11	0.0707
3	45.26	0.0729
3	45.56	0.0734
7	42.67	0.0662
7	43.24	0.0670
14	38.29	0.0542

14	39.19	0.0560
21	34.53	0.0478
21	35.04	0.0493
30	30.38	0.0408
30	30.76	0.0414
59	21.01	0.0250
59	21.94	0.0264
120	11.26	0.0124
120	11.37	0.0131

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	29.6	0	10000	False
V_add	370.4	0	10000	False
cont_OC	0.018	0	10000	False
c_LR	1	0.1	10000	False
M_0	50.2	0	10000	True
ExpFre	0.868	0.01	1.3	False
KOC_EQ	92.2	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	54	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.04359)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	29.600	ml	System	Volume of liquid in moist soil
V_add	370.400	ml	System	Volume of liquid added
cont_OC	0.018	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	47.179	µg	System	Initial mass of pesticide
ExpFre	0.868	-	Sorption	Freundlich exponent 1/N
KOC_EQ	77.279	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.334	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.040	1/d	Sorption	Desorption rate coefficient
DT50_EQ	44.619	d	Sorption	Transformation half-life (20°C)

EVALUTATION

Complete Data Set

No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	2.141
Weighted ME (Chi²)	2.611
Coeff. of Det. (R²)	0.999
Model efficiency	0.999
Abs. deviation	10.741

Quadr. deviation	9.334	
SRMSE	0.027	
STE	0.016	

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R^2)	0.998	0.982
Model efficiency	0.997	0.981
Abs. deviation	10.707	0.034
Quadr. deviation	9.334	0.000
SRMSE	0.019	0.056
STE	0.016	0.033

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210	47.175	1.03522	0.00043
0.000	47.840	47.175	0.66522	0.00044
0.000	47.810	47.170	0.63958	0.00044
1.000	46.810	46.452	0.35837	0.00046
1.000	48.110	46.452	1.65837	0.00043
3.000	45.260	45.061	0.19890	0.00049
3.000	45.560	45.061	0.49890	0.00048
7.000	42.670	42.486	0.18397	0.00055
7.000	43.240	42.486	0.75397	0.00053
14.000	38.290	38.518	-0.22793	0.00068
14.000	39.190	38.518	0.67207	0.00065
21.000	34.530	35.098	-0.56818	0.00084
21.000	35.040	35.098	-0.05818	0.00081
30.000	30.380	31.322	-0.94184	0.00108
30.000	30.760	31.322	-0.56184	0.00106
59.000	21.010	22.236	-1.22572	0.00227
59.000	21.940	22.236	-0.29572	0.00208
120.000	11.260	11.234	0.02633	0.00789
120.000	11.370	11.234	0.13633	0.00774

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.089	0.079	0.00932	127.10211
0.000	0.082	0.079	0.00212	150.55139
0.000	0.082	0.079	0.00243	149.44913
1.000	0.071	0.077	-0.00580	196.15689
1.000	0.071	0.077	-0.00650	200.06042
3.000	0.073	0.073	-0.00022	188.16764
3.000	0.073	0.073	0.00028	185.61278
7.000	0.066	0.066	0.00026	228.18339
7.000	0.067	0.066	0.00106	222.76676

14.000	0.054	0.056	-0.00170	340.40931
14.000	0.056	0.056	0.00010	318.87755
21.000	0.048	0.048	-0.00042	437.66741
21.000	0.049	0.048	0.00108	411.43967
30.000	0.041	0.041	0.00007	600.73049
30.000	0.041	0.041	0.00067	583.44419
59.000	0.025	0.026	-0.00121	1600.00000
59.000	0.026	0.026	0.00019	1434.80257
120.000	0.012	0.012	0.00005	6503.64204
120.000	0.013	0.012	0.00075	5827.16625

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	47.175	0.079
1.000	46.452	0.077
2.000	45.747	0.075
3.000	45.061	0.073
4.000	44.392	0.071
5.000	43.740	0.069
6.000	43.103	0.068
7.000	42.482	0.066
8.000	41.876	0.064
9.000	41.284	0.063
10.000	40.705	0.061
11.000	40.139	0.060
12.000	39.586	0.058
13.000	39.044	0.057
14.000	38.515	0.056
15.000	37.996	0.055
16.000	37.489	0.053
17.000	36.991	0.052
18.000	36.504	0.051
19.000	36.026	0.050
20.000	35.558	0.049
21.000	35.098	0.048
22.000	34.647	0.047
23.000	34.205	0.046
24.000	33.771	0.045
25.000	33.344	0.045
26.000	32.926	0.044
27.000	32.514	0.043
28.000	32.110	0.042
29.000	31.712	0.041
30.000	31.322	0.041
31.000	30.938	0.040
32.000	30.560	0.039
33.000	30.188	0.039
34.000	29.822	0.038
35.000	29.463	0.037
36.000	29.108	0.037
37.000	28.759	0.036
38.000	28.416	0.036
39.000	28.078	0.035
40.000	27.745	0.035
41.000	27.416	0.034
42.000	27.093	0.033
43.000	26.774	0.033

44.000	26.460	0.032
45.000	26.151	0.032
46.000	25.846	0.031
47.000	25.545	0.031
48.000	25.248	0.031
49.000	24.955	0.030
50.000	24.667	0.030
51.000	24.382	0.029
52.000	24.101	0.029
53.000	23.824	0.028
54.000	23.550	0.028
55.000	23.280	0.028
56.000	23.014	0.027
57.000	22.751	0.027
58.000	22.492	0.027
59.000	22.236	0.026
60.000	21.983	0.026
61.000	21.733	0.026
62.000	21.487	0.025
63.000	21.243	0.025
64.000	21.003	0.025
65.000	20.766	0.024
66.000	20.531	0.024
67.000	20.300	0.024
68.000	20.071	0.023
69.000	19.845	0.023
70.000	19.622	0.023
71.000	19.402	0.022
72.000	19.184	0.022
73.000	18.969	0.022
74.000	18.756	0.022
75.000	18.546	0.021
76.000	18.339	0.021
77.000	18.134	0.021
78.000	17.931	0.021
79.000	17.731	0.020
80.000	17.533	0.020
81.000	17.338	0.020
82.000	17.145	0.020
83.000	16.954	0.019
84.000	16.765	0.019
85.000	16.578	0.019
86.000	16.394	0.019
87.000	16.212	0.018
88.000	16.032	0.018
89.000	15.854	0.018
90.000	15.678	0.018
91.000	15.504	0.017
92.000	15.332	0.017
93.000	15.162	0.017
94.000	14.994	0.017
95.000	14.828	0.017
96.000	14.663	0.016
97.000	14.501	0.016
98.000	14.341	0.016
99.000	14.182	0.016

100.000	14.025	0.016
101.000	13.870	0.015
102.000	13.717	0.015
103.000	13.565	0.015
104.000	13.415	0.015
105.000	13.267	0.015
106.000	13.120	0.015
107.000	12.976	0.014
108.000	12.832	0.014
109.000	12.691	0.014
110.000	12.551	0.014
111.000	12.412	0.014
112.000	12.275	0.014
113.000	12.140	0.013
114.000	12.006	0.013
115.000	11.874	0.013
116.000	11.743	0.013
117.000	11.613	0.013
118.000	11.485	0.013
119.000	11.359	0.012
120.000	11.234	0.012

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to $(1/observation)^2$.

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.11 ECPA-07 Soil C

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 18/02/2019
Date of this report: 10/05/2019 10:08

Study: ECPA-07B
Description: Appendix C in EFSA PPR Panel 2018

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)

0	48.21	0.0887
0	47.79	0.0661
0	47.83	0.0657
1	48.66	0.0595
1	48.69	0.0562
3	46.08	0.0549
3	46.31	0.0561
7	44.39	0.0494
7	44.61	0.0487
14	41.36	0.0411
14	41.32	0.0412
21	40.11	0.0361
21	39.78	0.0369
30	37.22	0.0329
30	37.31	0.0326
59	31.63	0.0237
59	31.80	0.0238
120	25.39	0.0164
120	25.05	0.0178

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	31.4	0	10000	False
V_add	368.6	0	10000	False
cont_OC	0.023	0	10000	False
c_LR	1	0.1	10000	False
M_0	50.2	0	10000	True
ExpFre	0.864	0.01	1.3	False
KOC_EQ	107	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	157.5	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.11630)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	31.400	ml	System	Volume of liquid in moist soil
V_add	368.600	ml	System	Volume of liquid added
cont_OC	0.023	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration
M_0	47.100	µg	System	Initial mass of pesticide
ExpFre	0.864	-	Sorption	Freundlich exponent 1/N
KOC_EQ	98.806	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.749	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.041	1/d	Sorption	Desorption rate coefficient
DT50_EQ	77.023	d	Sorption	Transformation half-life (20°C)

EVALUTATION

Complete Data Set	
No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	3.314
Weighted ME (Chi²)	3.792
Coeff. of Det. (R²)	0.999
Model efficiency	0.999
Abs. deviation	17.317
Quadr. deviation	21.003
SRMSE	0.036
STE	0.022

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R²)	0.981	0.901
Model efficiency	0.980	0.897
Abs. deviation	17.267	0.050
Quadr. deviation	21.003	0.001
SRMSE	0.026	0.131
STE	0.022	0.059

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210	47.097	1.11262	0.00043
0.000	47.790	47.097	0.69262	0.00044
0.000	47.830	47.095	0.73514	0.00044
1.000	48.660	46.681	1.97875	0.00042
1.000	48.690	46.681	2.00875	0.00042
3.000	46.080	45.892	0.18791	0.00047
3.000	46.310	45.892	0.41791	0.00047
7.000	44.390	44.464	-0.07356	0.00051
7.000	44.610	44.464	0.14644	0.00050
14.000	41.360	42.319	-0.95898	0.00058
14.000	41.320	42.319	-0.99898	0.00059
21.000	40.110	40.487	-0.37740	0.00062
21.000	39.780	40.487	-0.70740	0.00063
30.000	37.220	38.430	-1.20954	0.00072
30.000	37.310	38.430	-1.11954	0.00072
59.000	31.630	32.964	-1.33382	0.00100
59.000	31.800	32.964	-1.16382	0.00099
120.000	25.390	24.198	1.19204	0.00155
120.000	25.050	24.198	0.85204	0.00159

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.089	0.065	0.02417	127.10211
0.000	0.066	0.065	0.00157	228.87433
0.000	0.066	0.065	0.00119	231.66971
1.000	0.060	0.062	-0.00257	282.46593
1.000	0.056	0.062	-0.00587	316.61200
3.000	0.055	0.058	-0.00273	331.78390
3.000	0.056	0.058	-0.00153	317.74175
7.000	0.049	0.050	-0.00100	409.77561
7.000	0.049	0.050	-0.00170	421.64026
14.000	0.041	0.042	-0.00048	591.99271
14.000	0.041	0.042	-0.00038	589.12244
21.000	0.036	0.036	0.00020	767.33604
21.000	0.037	0.036	0.00100	734.42469
30.000	0.033	0.031	0.00164	923.86434
30.000	0.033	0.031	0.00134	940.94622
59.000	0.024	0.024	-0.00048	1780.34147
59.000	0.024	0.024	-0.00038	1765.41205
120.000	0.016	0.017	-0.00067	3718.02499
120.000	0.018	0.017	0.00073	3156.16715

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	47.097	0.065
1.000	46.681	0.062
2.000	46.280	0.060
3.000	45.892	0.058
4.000	45.517	0.056
5.000	45.154	0.054
6.000	44.803	0.052
7.000	44.462	0.050
8.000	44.130	0.049
9.000	43.808	0.047
10.000	43.495	0.046
11.000	43.189	0.045
12.000	42.892	0.044
13.000	42.601	0.043
14.000	42.317	0.042
15.000	42.040	0.041
16.000	41.768	0.040
17.000	41.502	0.039
18.000	41.241	0.038
19.000	40.985	0.037
20.000	40.734	0.037
21.000	40.487	0.036
22.000	40.245	0.035
23.000	40.006	0.035
24.000	39.771	0.034
25.000	39.540	0.034
26.000	39.312	0.033
27.000	39.087	0.033
28.000	38.865	0.032
29.000	38.646	0.032
30.000	38.430	0.031
31.000	38.216	0.031
32.000	38.005	0.030
33.000	37.796	0.030

34.000	37.589	0.030
35.000	37.385	0.029
36.000	37.183	0.029
37.000	36.982	0.029
38.000	36.784	0.029
39.000	36.587	0.028
40.000	36.392	0.028
41.000	36.199	0.028
42.000	36.008	0.027
43.000	35.818	0.027
44.000	35.630	0.027
45.000	35.443	0.027
46.000	35.258	0.027
47.000	35.074	0.026
48.000	34.891	0.026
49.000	34.710	0.026
50.000	34.530	0.026
51.000	34.351	0.026
52.000	34.174	0.025
53.000	33.998	0.025
54.000	33.823	0.025
55.000	33.649	0.025
56.000	33.476	0.025
57.000	33.304	0.025
58.000	33.133	0.024
59.000	32.964	0.024
60.000	32.795	0.024
61.000	32.628	0.024
62.000	32.461	0.024
63.000	32.296	0.024
64.000	32.131	0.023
65.000	31.968	0.023
66.000	31.805	0.023
67.000	31.643	0.023
68.000	31.482	0.023
69.000	31.322	0.023
70.000	31.163	0.023
71.000	31.005	0.022
72.000	30.848	0.022
73.000	30.692	0.022
74.000	30.536	0.022
75.000	30.381	0.022
76.000	30.228	0.022
77.000	30.075	0.022
78.000	29.922	0.022
79.000	29.771	0.021
80.000	29.621	0.021
81.000	29.471	0.021
82.000	29.322	0.021
83.000	29.174	0.021
84.000	29.026	0.021
85.000	28.880	0.021
86.000	28.734	0.021
87.000	28.589	0.020
88.000	28.444	0.020
89.000	28.301	0.020

90.000	28.158	0.020
91.000	28.016	0.020
92.000	27.875	0.020
93.000	27.734	0.020
94.000	27.594	0.020
95.000	27.455	0.020
96.000	27.316	0.019
97.000	27.179	0.019
98.000	27.042	0.019
99.000	26.905	0.019
100.000	26.770	0.019
101.000	26.635	0.019
102.000	26.500	0.019
103.000	26.367	0.019
104.000	26.234	0.019
105.000	26.102	0.019
106.000	25.970	0.018
107.000	25.840	0.018
108.000	25.709	0.018
109.000	25.580	0.018
110.000	25.451	0.018
111.000	25.323	0.018
112.000	25.195	0.018
113.000	25.068	0.018
114.000	24.942	0.018
115.000	24.816	0.018
116.000	24.692	0.017
117.000	24.567	0.017
118.000	24.443	0.017
119.000	24.320	0.017
120.000	24.198	0.017

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to $(1/observation)^2$.

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

A.1.12 ECPA-07 Soil D

SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018

Version: 18/02/2019
Date of this report: 10/05/2019 09:57

Study: ECPA-07D
Description: Appendix C in EFSA PPR Panel 2018

INPUT DATA

Experimental Data

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0	48.21	0.0887
0	46.97	0.0537
0	46.57	0.0544
1	44.20	0.0503
1	45.67	0.0491
3	45.37	0.0487
3	44.87	0.0490
7	43.21	0.0436
7	43.20	0.0437
14	37.97	0.0365
14	38.30	0.0364
21	34.26	0.0314
21	33.96	0.0321
30	31.69	0.0269
30	31.73	0.0270
59	22.90	0.0170
59	23.42	0.0168
120	14.31	0.0089
120	14.50	0.0089

Parameters

Name	Initial Value	Lower Bound	Upper Bound	Fit
M_sol	100	0	10000	False
V_sol	45.9	0	10000	False
V_add	354.1	0	10000	False
cont_OC	0.046	0	10000	False
c_LR	1	0.1	10000	False
M_0	50.2	0	10000	True
ExpFre	0.865	0.01	1.3	False
KOC_EQ	74.9	0	10000	True
f_NEQ	0.2	0	10000	True
k_des	0.05	0	0.5	True
DT50_EQ	50.4	0	10000	True

OUTPUT DATA

Result of parameter fitting (objective function value: 0.17539)

Parameter	Value	Unit	Category	Description
M_sol	100.000	g	System	Mass of dry soil
V_sol	45.900	ml	System	Volume of liquid in moist soil
V_add	354.100	ml	System	Volume of liquid added
cont_OC	0.046	kg/kg	System	Organic carbon content
c_LR	1.000	mg/l	Sorption	Reference concentration

M_0	46.087	µg	System	Initial mass of pesticide
ExpFre	0.865	-	Sorption	Freundlich exponent 1/N
KOC_EQ	64.680	l/kg	Sorption	Equilibrium KOC
f_NEQ	0.516	-	Sorption	Ratio Kf,neq/Kf,eq
k_des	0.032	1/d	Sorption	Desorption rate coefficient
DT50_EQ	48.065	d	Sorption	Transformation half-life (20°C)

EVALUTATION

Complete Data Set	
No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	3.150
Weighted ME (Chi²)	4.228
Coeff. of Det. (R²)	0.999
Model efficiency	0.999
Abs. deviation	15.910
Quadr. deviation	18.530
SRMSE	0.038
STE	0.023

	Total mass (µg)		Conc liq. phase (µg/mL)	
No obs.	19	19		
Coeff. of Det. (R²)	0.992	0.830		
Model efficiency	0.991	0.821		
Abs. deviation	15.860	0.050		
Quadr. deviation	18.529	0.001		
SRMSE	0.027	0.207		
STE	0.023	0.070		

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210	46.082	2.12841	0.00043
0.000	46.970	46.082	0.88841	0.00045
0.000	46.570	46.076	0.49395	0.00046
1.000	44.200	45.427	-1.22656	0.00051
1.000	45.670	45.427	0.24344	0.00048
3.000	45.370	44.171	1.19891	0.00049
3.000	44.870	44.171	0.69891	0.00050
7.000	43.210	41.862	1.34796	0.00054
7.000	43.200	41.862	1.33796	0.00054
14.000	37.970	38.335	-0.36548	0.00069
14.000	38.300	38.335	-0.03548	0.00068

21.000	34.260	35.337	-1.07723	0.00085
21.000	33.960	35.337	-1.37723	0.00087
30.000	31.690	32.053	-0.36285	0.00100
30.000	31.730	32.053	-0.32285	0.00099
59.000	22.900	24.161	-1.26123	0.00191
59.000	23.420	24.161	-0.74123	0.00182
120.000	14.310	14.029	0.28076	0.00488
120.000	14.500	14.029	0.47076	0.00476

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.089	0.055	0.03385	127.10211
0.000	0.054	0.055	-0.00115	346.77791
0.000	0.054	0.055	-0.00043	337.91090
1.000	0.050	0.053	-0.00287	395.24286
1.000	0.049	0.053	-0.00407	414.79835
3.000	0.049	0.050	-0.00134	421.64026
3.000	0.049	0.050	-0.00104	416.49313
7.000	0.044	0.045	-0.00100	526.05000
7.000	0.044	0.045	-0.00090	523.64520
14.000	0.037	0.037	-0.00059	750.60987
14.000	0.036	0.037	-0.00069	754.73977
21.000	0.031	0.032	-0.00012	1014.23993
21.000	0.032	0.032	0.00058	970.48748
30.000	0.027	0.026	0.00063	1381.95990
30.000	0.027	0.026	0.00073	1371.74211
59.000	0.017	0.017	0.00008	3460.20761
59.000	0.017	0.017	-0.00012	3543.08390
120.000	0.009	0.009	0.00005	12624.66860
120.000	0.009	0.009	0.00005	12624.66860

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)
0.000	46.082	0.055
1.000	45.427	0.053
2.000	44.790	0.052
3.000	44.171	0.050
4.000	43.569	0.049
5.000	42.983	0.047
6.000	42.413	0.046
7.000	41.857	0.045
8.000	41.316	0.043
9.000	40.789	0.042
10.000	40.274	0.041
11.000	39.772	0.040
12.000	39.282	0.039
13.000	38.803	0.038
14.000	38.335	0.037
15.000	37.879	0.036
16.000	37.432	0.035
17.000	36.995	0.035
18.000	36.567	0.034
19.000	36.149	0.033
20.000	35.739	0.032
21.000	35.337	0.032
22.000	34.944	0.031

23.000	34.558	0.030
24.000	34.180	0.030
25.000	33.809	0.029
26.000	33.445	0.028
27.000	33.087	0.028
28.000	32.736	0.027
29.000	32.392	0.027
30.000	32.053	0.026
31.000	31.720	0.026
32.000	31.393	0.025
33.000	31.071	0.025
34.000	30.754	0.024
35.000	30.443	0.024
36.000	30.136	0.024
37.000	29.834	0.023
38.000	29.537	0.023
39.000	29.244	0.022
40.000	28.956	0.022
41.000	28.672	0.022
42.000	28.392	0.021
43.000	28.116	0.021
44.000	27.843	0.021
45.000	27.575	0.020
46.000	27.310	0.020
47.000	27.049	0.020
48.000	26.791	0.020
49.000	26.537	0.019
50.000	26.286	0.019
51.000	26.038	0.019
52.000	25.793	0.019
53.000	25.551	0.018
54.000	25.313	0.018
55.000	25.077	0.018
56.000	24.844	0.018
57.000	24.614	0.017
58.000	24.386	0.017
59.000	24.161	0.017
60.000	23.939	0.017
61.000	23.719	0.017
62.000	23.502	0.016
63.000	23.287	0.016
64.000	23.075	0.016
65.000	22.865	0.016
66.000	22.657	0.016
67.000	22.452	0.015
68.000	22.249	0.015
69.000	22.047	0.015
70.000	21.849	0.015
71.000	21.652	0.015
72.000	21.457	0.014
73.000	21.264	0.014
74.000	21.073	0.014
75.000	20.885	0.014
76.000	20.698	0.014
77.000	20.513	0.014
78.000	20.330	0.014

79.000	20.148	0.013
80.000	19.969	0.013
81.000	19.791	0.013
82.000	19.615	0.013
83.000	19.441	0.013
84.000	19.269	0.013
85.000	19.098	0.013
86.000	18.929	0.012
87.000	18.761	0.012
88.000	18.595	0.012
89.000	18.431	0.012
90.000	18.268	0.012
91.000	18.107	0.012
92.000	17.947	0.012
93.000	17.789	0.012
94.000	17.632	0.011
95.000	17.477	0.011
96.000	17.323	0.011
97.000	17.171	0.011
98.000	17.020	0.011
99.000	16.871	0.011
100.000	16.723	0.011
101.000	16.576	0.011
102.000	16.430	0.011
103.000	16.286	0.010
104.000	16.144	0.010
105.000	16.002	0.010
106.000	15.862	0.010
107.000	15.723	0.010
108.000	15.586	0.010
109.000	15.449	0.010
110.000	15.314	0.010
111.000	15.180	0.010
112.000	15.048	0.010
113.000	14.916	0.009
114.000	14.786	0.009
115.000	14.657	0.009
116.000	14.529	0.009
117.000	14.402	0.009
118.000	14.276	0.009
119.000	14.152	0.009
120.000	14.028	0.009

The objective function is based on weighted least squares of observed data and by model predicted data.
The weight for each data point is equal to $(1/\text{observation})^2$.

The calibration was done using the Nelder Mead solver by Microsoft Solver Foundation. The implementation of the solver implements the method described in Nelder, J.A. and Mead, R., "A Simplex Method for Function Minimization", Computer Journal 7 (4): 308-313 (Jan., 1965) with the modifications described in Lee, D. and Wiswall, M., "A Parallel Implementation of the Simplex Function Minimization Routine".

8 Abbreviations and definitions

Definitions (taken from EFSA PPR Panel 2018).

Term	Definition
Aged sorption	Increased sorption after extended contact between pesticide and soil
Aged sorption study	An incubation study whereby sorption is measured at different time intervals after application of the test substance
Batch sorption study	A sorption study in which soils are shaken with pesticide solution for a certain period of time
Equilibrium domain	The liquid phase and the equilibrium sorption sites together
Equilibrium sorption sites	Locations in the soil where sorption occurs rapidly. In the two-site model this part of sorption is assumed to reach equilibrium instantaneously, while non-equilibrium sorption is the additional sorption that takes place with prolonged contact time. The cut-off between equilibrium and non-equilibrium sorption is arbitrary. Here equilibrium sorption is defined as the sorption that would occur after the soil is shaken with pesticide solution for 24 h
Non-equilibrium sorption sites	Locations in the soil where sorption occurs with time, when the pesticide is exposed to the soil for a longer period. See also the description of 'Equilibrium sorption sites'. In this guidance nonequilibrium sorption is defined as the sorption that occurs beyond equilibrium sorption
Recovery	The percentage of test compound that can be recovered from the soil by extraction
Two-site model	A model that describes sorption at two types of sorption sites: equilibrium sites and non-equilibrium sites. Sorption at the equilibrium sites is assumed to reach equilibrium instantaneously, while adsorption and desorption at the non-equilibrium sites take time to reach equilibrium