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SORPKINANALYSIS 1.1

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-0, ECPA-06 and 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. Addionally, SorpKinAnalysis 1.0 was tested by Mike Fuchs in 2019. The result of the analysis can be found at the download area http://software.ime.fraunhofer.de/SorpKinAnalysis/.

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}).

Groundwater risk assessment

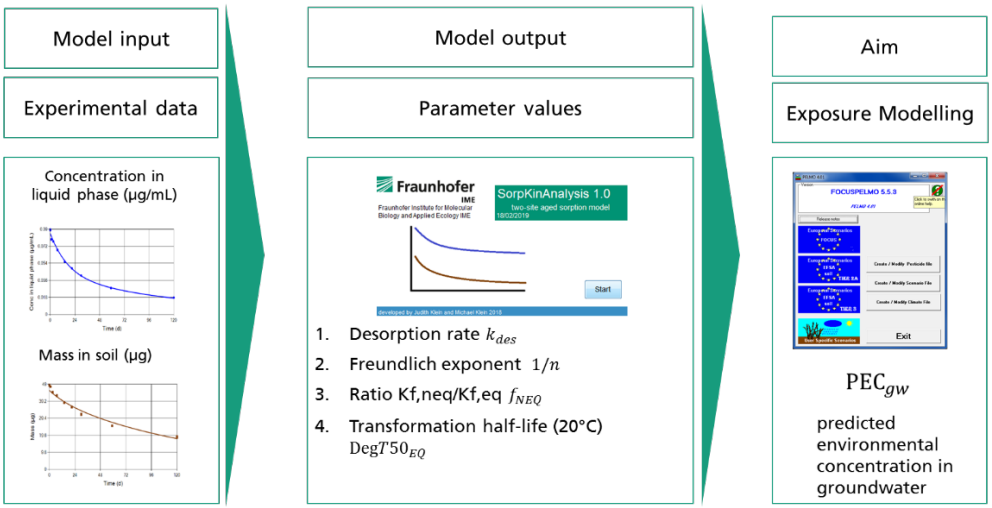

Figure 1: Schematic representation of the thematic background of SorpKinAnalysis.

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.

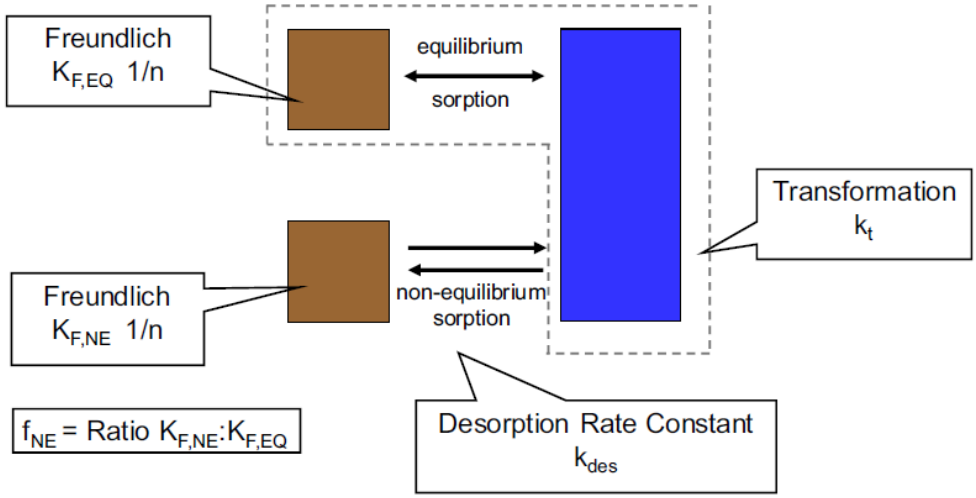

Figure 2: Schematic representation of the two-aged sorption model taken from EFSA PPR Panel 2018.

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).

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

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:

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

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

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

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.

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

In addition to that the apparent sorption coefficient $k_d(t)$ (mL/g) as ratio between total adsorbed concentration (µg/g) and the concentration in soil solution (µg/mL) is calculated.

$$k_d(t) = \frac{X_{EQ}(t) + X_{NEQ}(t)}{c_{liq}(t)}$$

The apparent distribution coefficient is often calculated to show the relevance of aged sorption (EFSA PPR Panel 2018). It is not used as a dependent variable in the fitting procedure.

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
$k_d: [0, t_n] \rightarrow \mathbb{R}_+$	KdApp	mL/g	ratio between total adsorbed concentration (µg/g) and the concentration in soil solution (µg/mL)

3 Parameter fitting

The objective implemented in the software SorpKinAnalysis 1.1 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 1.1 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.

The apparent distribution coefficient is not used as a dependent variable in the fitting procedure. It is only provided for additional evaluation of the fitting result.

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, liquid and the apparent distribution coefficient.

Additionally to the optimized parameter value the parameter's standard error and the 95% confidence interval is given to give an insight on the parameter's uncertainty. The calculation of confidence intervals is based on the calculation of covariance matrix. In some cases it is not possible to calculate the matrix. Then, no confidence intervals are provided. Note, that the calculated confidence intervals can be outside of the parameter's domain.

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).

The apparent distribution coefficient is often calculated to show the relevance of aged sorption. It shall be smaller than that for the equilibrium model (EFSA PPR Panel 2018).
The experimental apparent sorption coefficient $\mathrm{k}_{\mathrm{d}_{\mathrm{app}_\mathrm{i}}}$ is calculated for each measurement $i = 1, \cdots, n$ as follows:

$$\mathrm{k}_{\mathrm{d}_{\mathrm{app}_\mathrm{i}}} = \frac{\frac{M_i - (V_{add} + V_{sol}) \cdot c_{liq_i}}{M_{sol}}}{c_{liq_i}}$$

Table 6: Parameter used for calculation of apparent distribution coefficient 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
M_i	MasSol	g	Observed mass of dry soil
V_{sol}	VolLiqSol	ml	Volume of liquid in moist soil
V_{add}	VolLiqAdd	ml	Volume of liquid added
M_i	TotalMass	µg	Observed mass of substance in soil
c_{liq_i}	ConLiq	µg/ml	Observed concentration of substance in liquid phase

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).

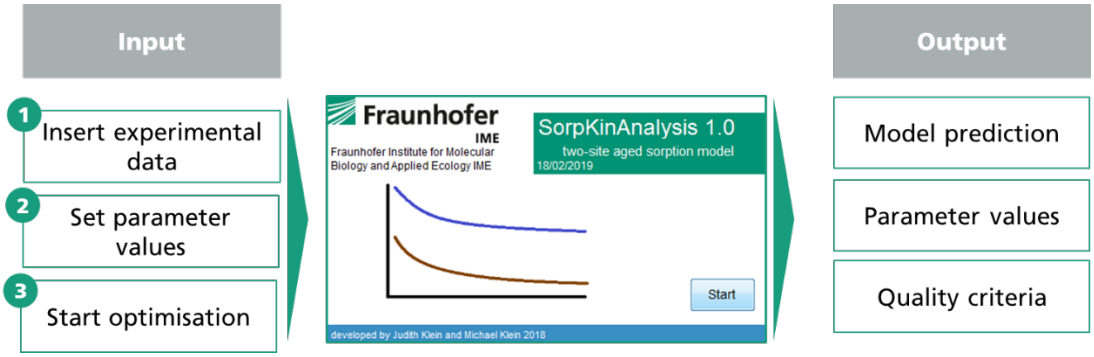

Figure 3: Schematic representation of the working procedure using SorpKinAnalysis.

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.

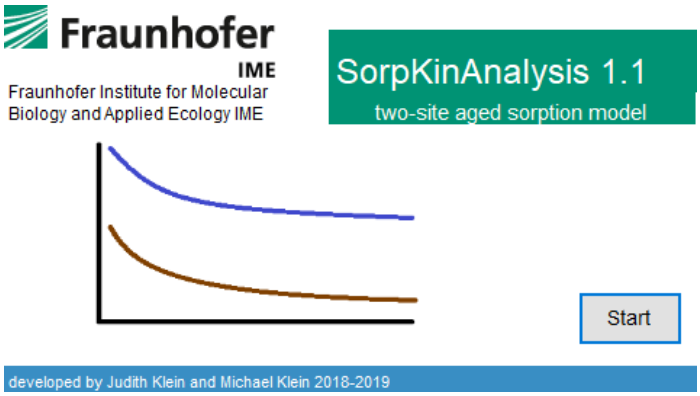

Figure 4: Start screen of the program SorpKinAnalysis 1.1

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.

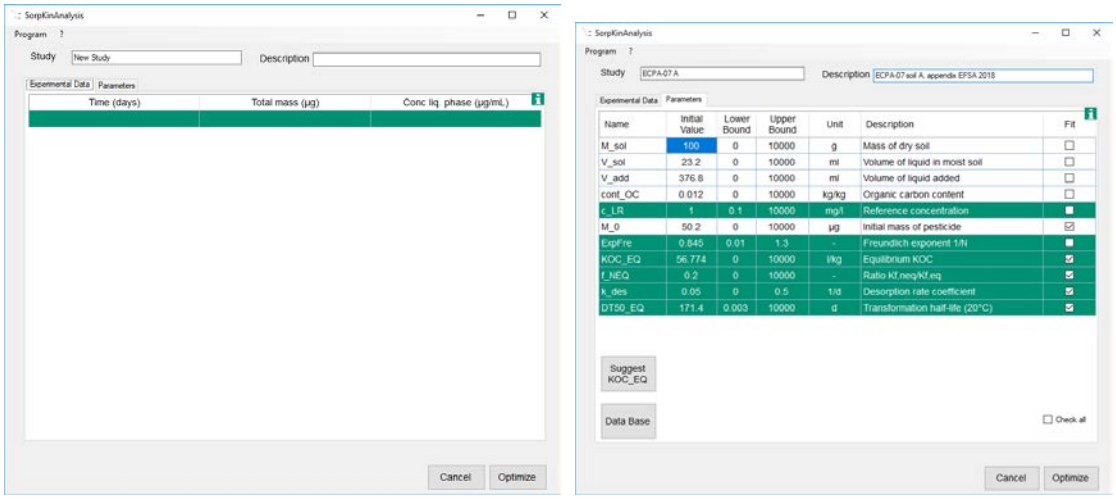

Figure 5: Main form of SorpKinAnalysis: Experimental data tab page (left) and parameters tab pages (right)

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.

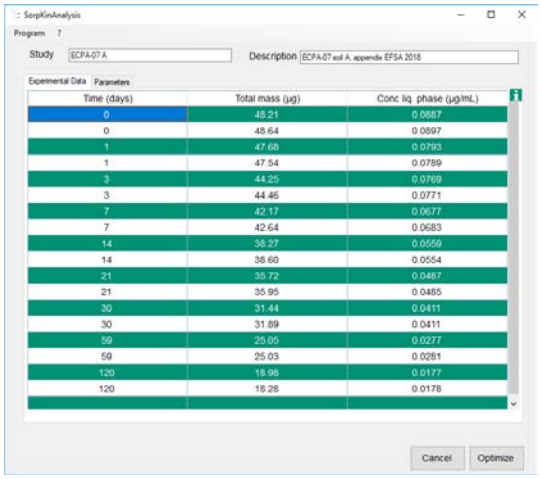

Figure 6: Experimental data in environmental residues tab page

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.

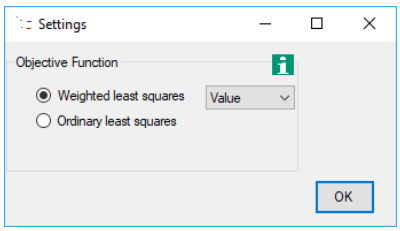

Figure 7: Settings of fitting routine

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, the change of pesticide concentration in liquid phase, the change of apparent distribution coefficient
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 and 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".

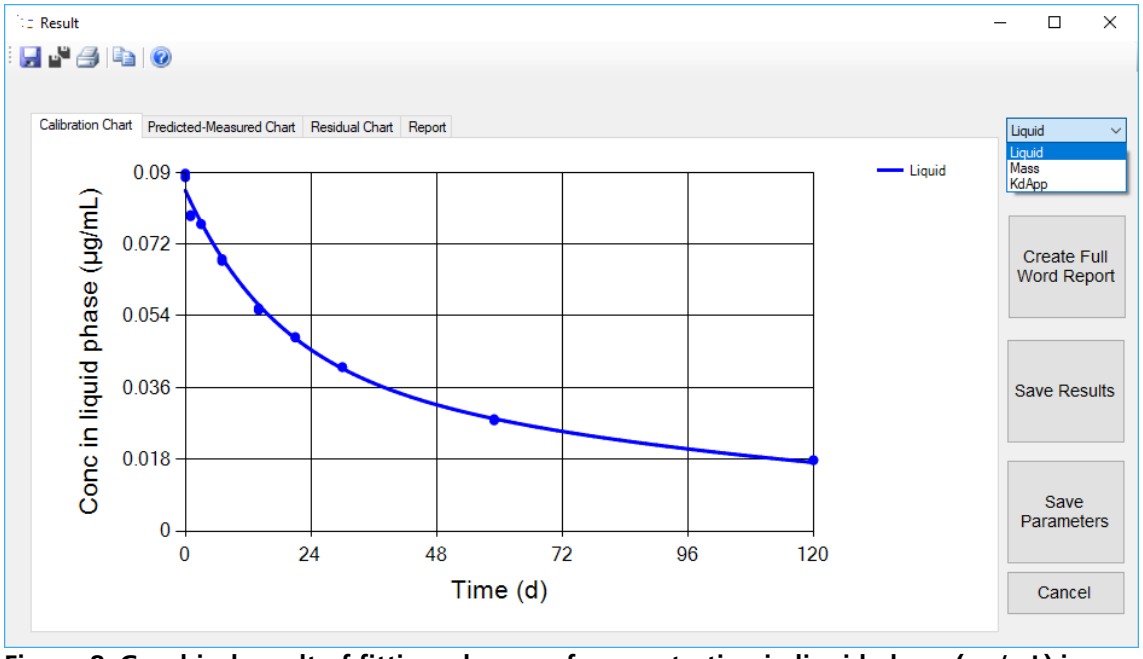

Figure 8: Graphical result of fitting, change of concentration in liquid phase (µg/mL) in time

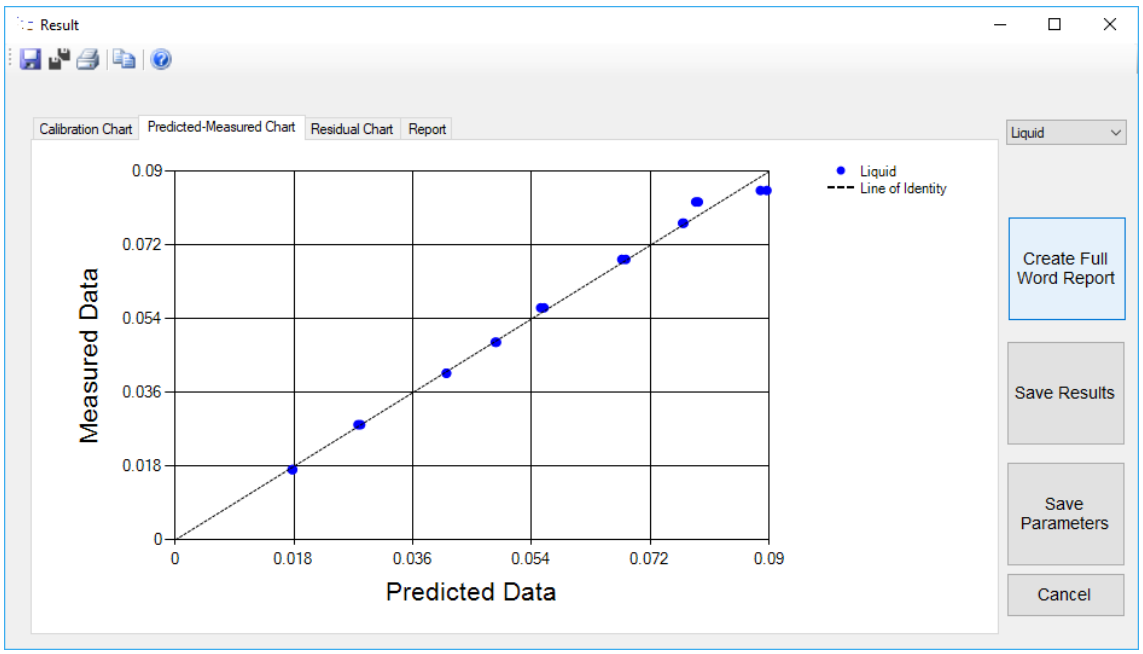

Figure 9: Predicted data versus measured data

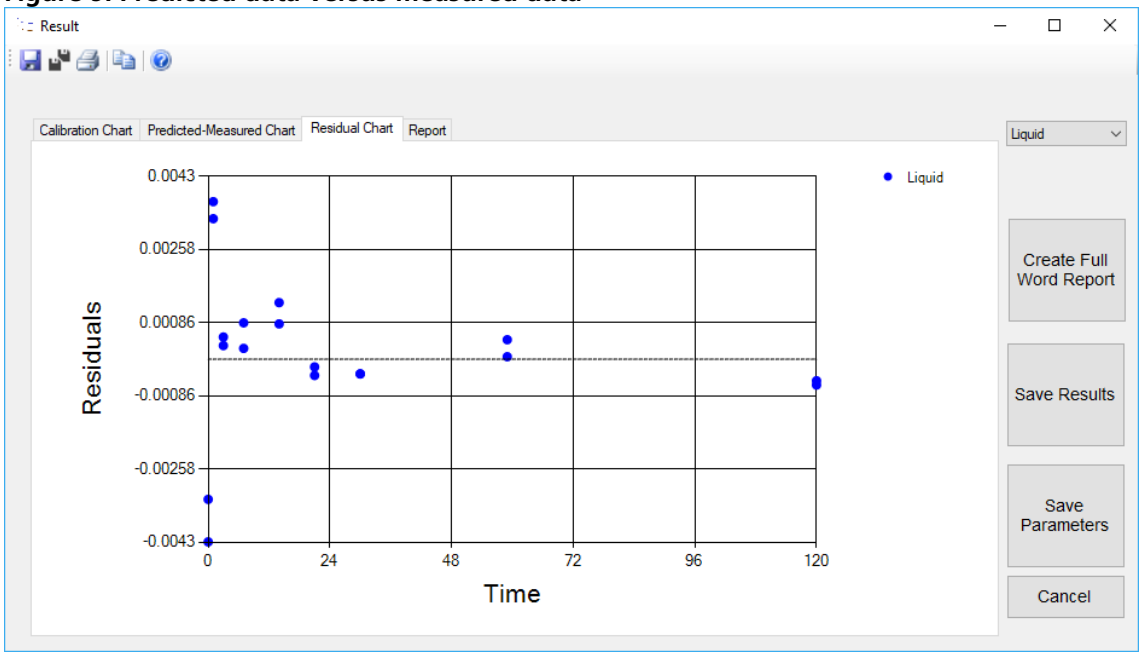

Figure 10: Time data versus residuals (predicted minus observed data)

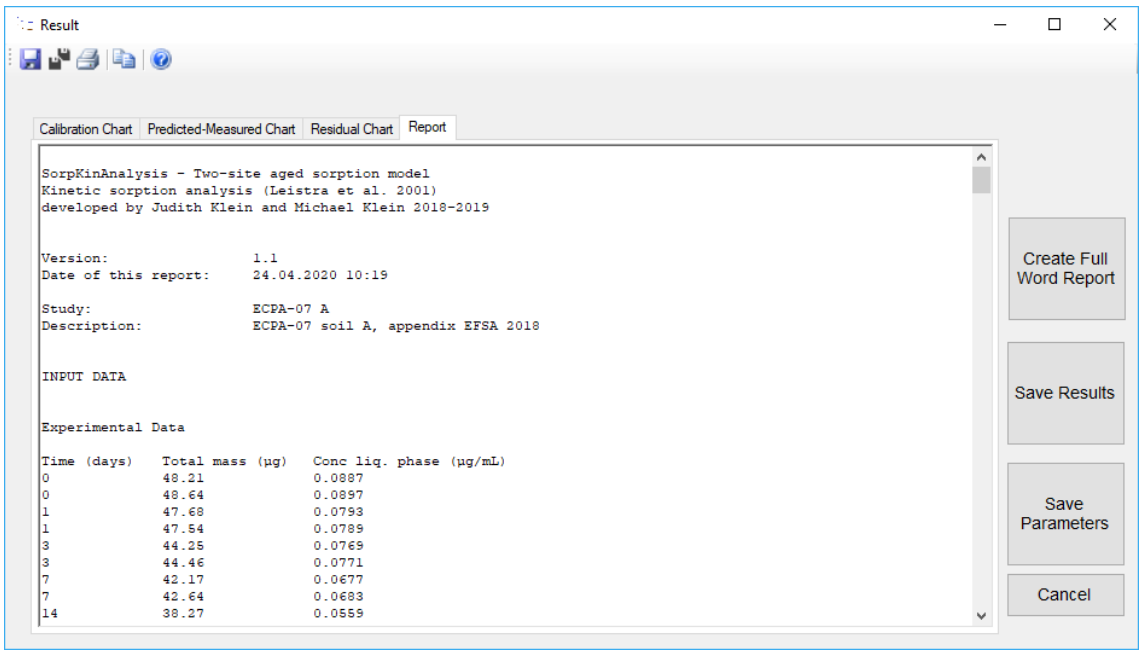

Figure 11: Text report file

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 12 contains the experimental data used for parameter fitting for each soil. Fitting is done separately for each soil.

Table 7: 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 13. 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 8: (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 1.1

The numeric parameter value result can be seen in Table 14. 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 9: Parameter values of fitted model parameters of ECPA-01 soil D E, F and G (EFSA PPR Panel 2018) using SorpKinAnalysis 1.1 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 14 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 12 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 13. 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 10: (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 1.1

The numeric parameter value result can be seen in Table 14. 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 11: Parameter values of fitted model parameters of ECPA-06 soil A, B, C and D (EFSA PPR Panel 2018) using SorpKinAnalysis 1.1 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 14 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 12 contains the experimental data used for parameter fitting for each soil. Fitting is done separately for each soil.

Table 12: 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 13. 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 13: (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 1.1

The numeric parameter value result can be seen in Table 14. 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 14: Parameter values of fitted model parameters of ECPA-07 soil A, B, C, and D (EFSA PPR Panel 2018) using SorpKinAnalysis 1.1 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 14 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 22, 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.

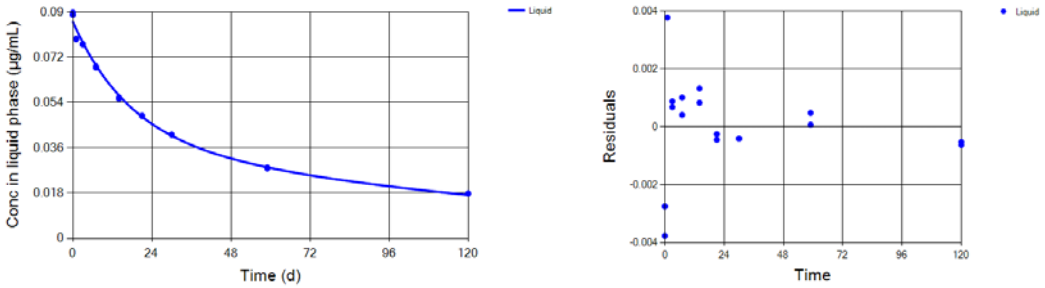

Figure 12: Soil A - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

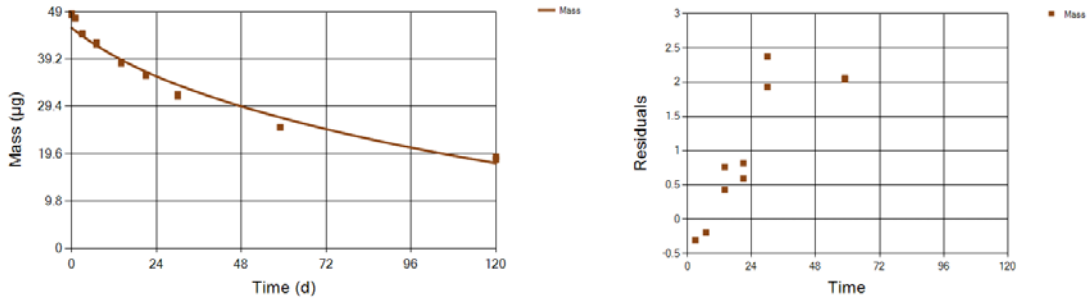

Figure 13: Soil A - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

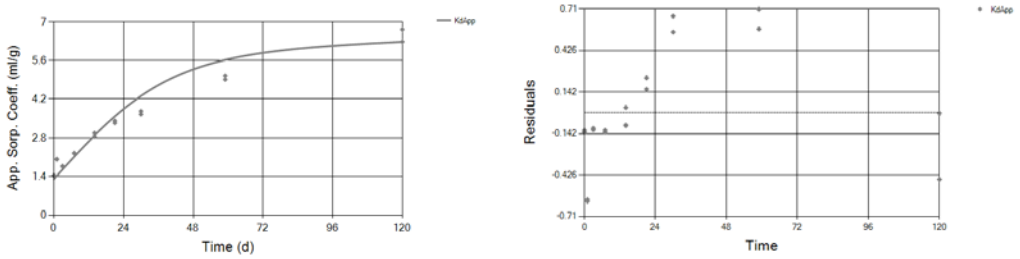

Figure 14: Soil A - Change of apparent sorption coefficient in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

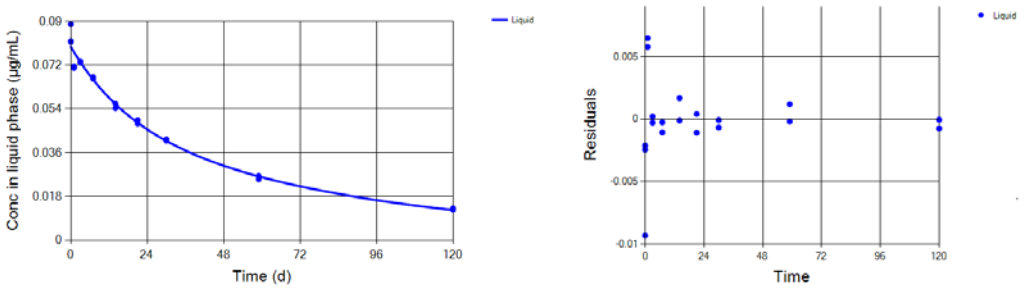

Figure 15: Soil B - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

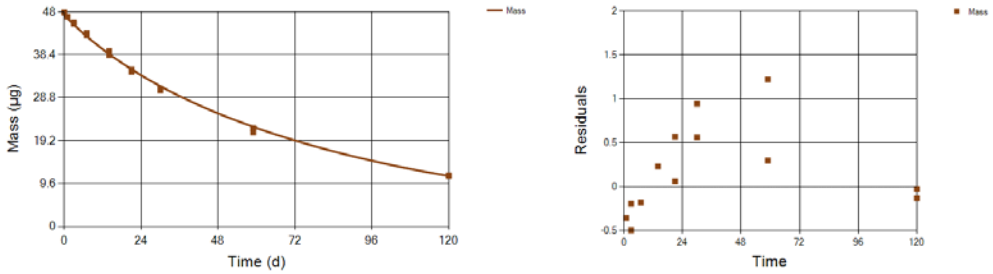

Figure 16: Soil B - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

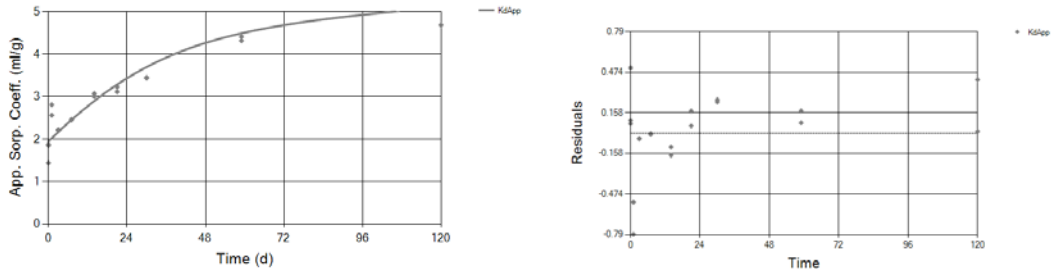

Figure 17: Soil B - Change of apparent sorption coefficient in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

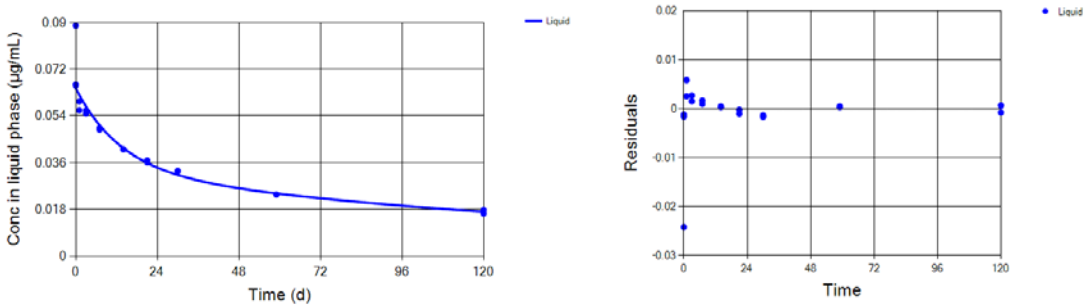

Figure 18: Soil C - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

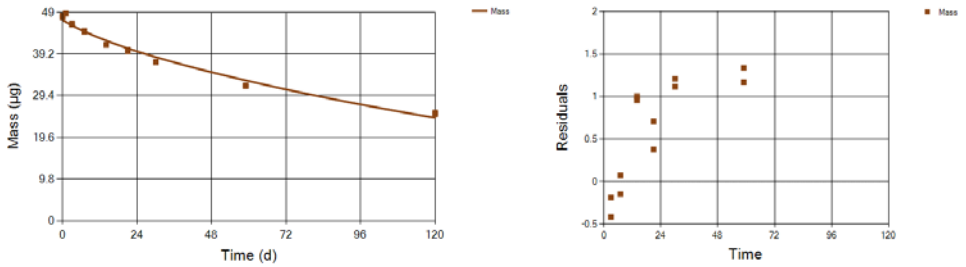

Figure 19: Soil C - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

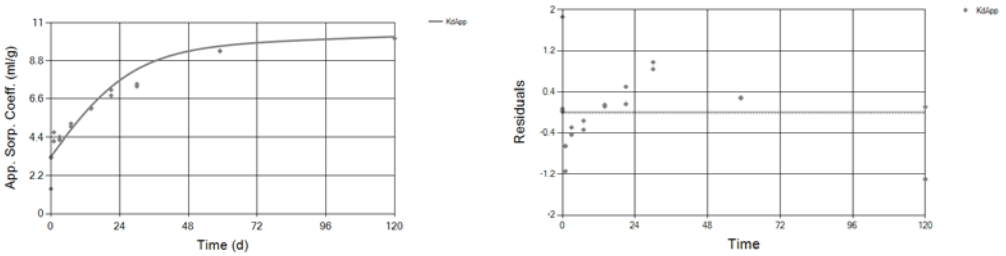

Figure 20: Soil C - Change of apparent sorption coefficient in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

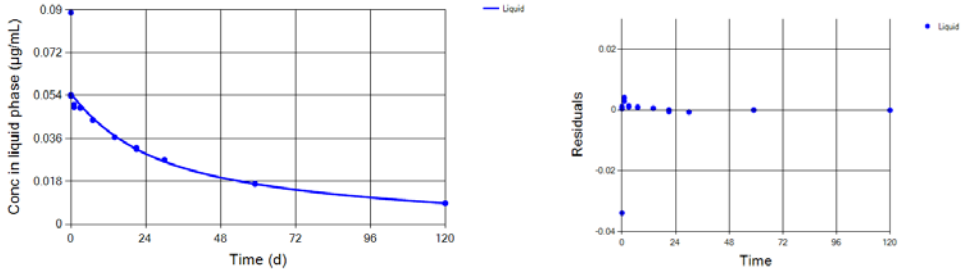

Figure 21: Soil D - Change of concentration in liquid phase in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

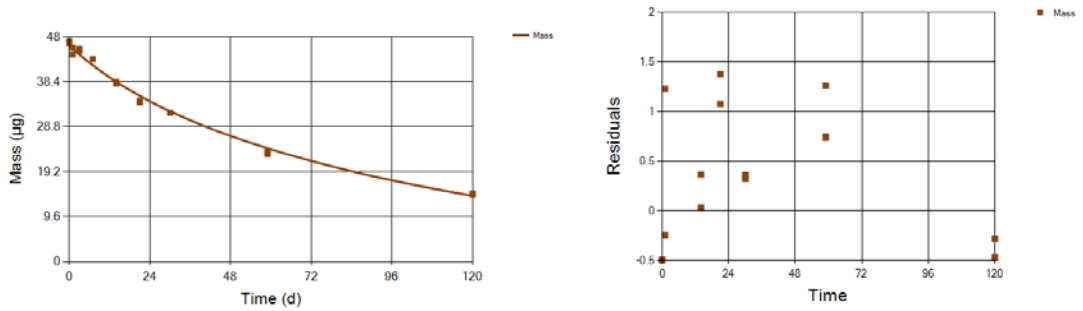

Figure 22: Soil D - Change of mass in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

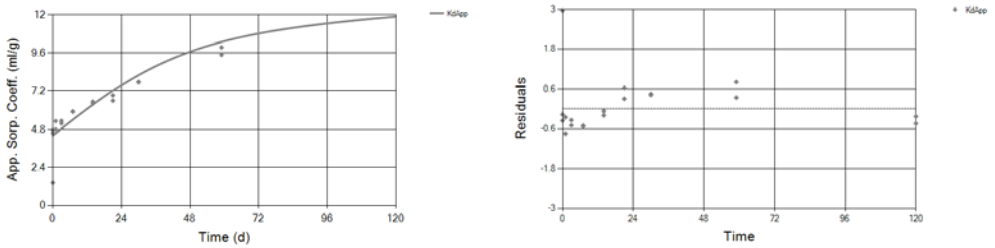

Figure 23: Soil D - Change of apparent sorption coefficient in time as well as a plot showing residuals using analytical data (predicted data) and approximate data (measured data).

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 1.1

A.1.1 ECPA-01 Soil D

```
SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  17.04.2020 15:55

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      0.003   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)

Parameter uncertainty
Parameter           Value     Standard Error     Prob > t
M_0         7.344334        0.003084        0.000000
KOC_EQ      8.983324        0.003814        0.000000
f_NEQ       0.581750        0.020818        0.000000
k_des       0.049925        0.134943        0.355775
DT50_EQ    79.460442        0.001095        0.000000

Parameter           Value     Lower Bound    Upper Bound
M_0         7.344334        7.338290        7.350378
KOC_EQ      8.983324        8.975848        8.990799
f_NEQ       0.581750        0.540946        0.622554
k_des       0.049925       -0.214563        0.314413
DT50_EQ    79.460442       79.458296       79.462588

Upper and lower bounds of parameter is not taken into account in the calculation of 95%
confidence intervals.


EVALUATION



       Complete Data Set
No obs. 32
No act. param. 5
Deg. of Freedom         11
Model error (Chi²)      4.994620
Weighted ME (Chi²)      2.801593
Coeff. of Det. (R²)     0.997314
Model efficiency        0.997117
Abs. deviation 3.531319
Quadr. deviation        0.973097
SRMSE   0.055954
```

STE 0.035409

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R^2)	0.978204	0.997596
Model efficiency	0.972289	0.997488
Abs. deviation	3.522508	0.008810
Quadr. deviation	0.973090	0.000007
SRMSE	0.039837	0.015432
STE	0.035563	0.012975

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R^2)	0.940211
Model efficiency	0.838913
Abs. deviation	0.814163
Quadr. deviation	0.051570
SRMSE	0.113095
STE	0.101367

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.620000	7.344001	0.275999	0.01722
0.000	7.620000	7.344001	0.275999	0.01722
1.000	7.730000	7.280990	0.449010	0.01674
1.000	7.640000	7.280990	0.359010	0.01713
3.000	7.320000	7.158429	0.161571	0.01866
3.000	7.350000	7.158429	0.191571	0.01851
7.000	6.940000	6.927677	0.012323	0.02076
7.000	7.090000	6.927677	0.162323	0.01989
14.000	6.440000	6.562760	-0.122760	0.02411
14.000	6.400000	6.562760	-0.162760	0.02441
30.000	5.580000	5.852005	-0.272005	0.03212
30.000	5.530000	5.852005	-0.322005	0.03270
58.000	4.560000	4.850331	-0.290331	0.04809
58.000	4.570000	4.850331	-0.280331	0.04788
120.000	3.360000	3.237746	0.122254	0.08858
120.000	3.300000	3.237746	0.062254	0.09183

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.057800	0.056903	0.000897	299.32592
0.000	0.056800	0.056903	-0.000103	309.95834
1.000	0.056100	0.055607	0.000493	317.74175
1.000	0.055900	0.055607	0.000293	320.01946
3.000	0.052700	0.053199	-0.000499	360.06323
3.000	0.051700	0.053199	-0.001499	374.12688

7.000	0.048300	0.049064	-0.000764	428.65287
7.000	0.048500	0.049064	-0.000564	425.12488
14.000	0.043800	0.043521	0.000279	521.25685
14.000	0.043500	0.043521	-0.000021	528.47140
30.000	0.035400	0.035556	-0.000156	797.98270
30.000	0.036100	0.035556	0.000544	767.33604
58.000	0.027500	0.027959	-0.000459	1322.31405
58.000	0.027100	0.027959	-0.000859	1361.63723
120.000	0.019000	0.018210	0.000790	2770.08310
120.000	0.018800	0.018210	0.000590	2829.33454

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	0.318339	0.290680	0.027659	299.32592
0.000000	0.341549	0.290680	0.050869	309.95834
1.000000	0.377897	0.309430	0.068466	317.74175
1.000000	0.366726	0.309430	0.057296	320.01946
3.000000	0.388994	0.345651	0.043344	360.06323
3.000000	0.421663	0.345651	0.076013	374.12688
7.000000	0.436853	0.412023	0.024830	428.65287
7.000000	0.461856	0.412023	0.049833	425.12488
14.000000	0.470320	0.508027	-0.037707	521.25685
14.000000	0.471264	0.508027	-0.036762	528.47140
30.000000	0.576271	0.645936	-0.069665	797.98270
30.000000	0.531856	0.645936	-0.114080	767.33604
58.000000	0.658182	0.734884	-0.076703	1322.31405
58.000000	0.686347	0.734884	-0.048537	1361.63723
120.000000	0.768421	0.778069	-0.009648	2770.08310
120.000000	0.755319	0.778069	-0.022750	2829.33454

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	7.344001	0.056903	0.290680
1.000000	7.280663	0.055600	0.309527
2.000000	7.218726	0.054365	0.327885
3.000000	7.158117	0.053193	0.345742
4.000000	7.098768	0.052081	0.363090
5.000000	7.040618	0.051024	0.379922
6.000000	6.983606	0.050020	0.396234
7.000000	6.927677	0.049064	0.412023
8.000000	6.872779	0.048155	0.427289
9.000000	6.818864	0.047288	0.442033
10.000000	6.765884	0.046463	0.456259
11.000000	6.713798	0.045675	0.469971
12.000000	6.662564	0.044923	0.483175
13.000000	6.612144	0.044204	0.495878
14.000000	6.562504	0.043517	0.508089
15.000000	6.513608	0.042860	0.519817
16.000000	6.465426	0.042230	0.531073
17.000000	6.417928	0.041626	0.541867
18.000000	6.371086	0.041047	0.552211
19.000000	6.324874	0.040491	0.562118
20.000000	6.279267	0.039956	0.571599
21.000000	6.234243	0.039442	0.580668
22.000000	6.189778	0.038947	0.589339

23.000000	6.145854	0.038470	0.597623
24.000000	6.102449	0.038010	0.605535
25.000000	6.059547	0.037566	0.613089
26.000000	6.017131	0.037137	0.620297
27.000000	5.975183	0.036723	0.627173
28.000000	5.933689	0.036321	0.633729
29.000000	5.892634	0.035932	0.639980
30.000000	5.852005	0.035556	0.645936
31.000000	5.811790	0.035190	0.651612
32.000000	5.771976	0.034835	0.657019
33.000000	5.732551	0.034490	0.662168
34.000000	5.693505	0.034154	0.667072
35.000000	5.654829	0.033827	0.671742
36.000000	5.616511	0.033509	0.676188
37.000000	5.578544	0.033198	0.680421
38.000000	5.540919	0.032896	0.684450
39.000000	5.503626	0.032600	0.688287
40.000000	5.466660	0.032311	0.691939
41.000000	5.430012	0.032029	0.695417
42.000000	5.393676	0.031752	0.698728
43.000000	5.357645	0.031482	0.701882
44.000000	5.321913	0.031217	0.704885
45.000000	5.286473	0.030957	0.707746
46.000000	5.251320	0.030702	0.710472
47.000000	5.216450	0.030452	0.713070
48.000000	5.181856	0.030206	0.715547
49.000000	5.147534	0.029965	0.717909
50.000000	5.113479	0.029728	0.720161
51.000000	5.079686	0.029494	0.722310
52.000000	5.046153	0.029265	0.724362
53.000000	5.012873	0.029039	0.726321
54.000000	4.979845	0.028816	0.728192
55.000000	4.947063	0.028597	0.729980
56.000000	4.914525	0.028381	0.731691
57.000000	4.882226	0.028168	0.733326
58.000000	4.850164	0.027958	0.734892
59.000000	4.818336	0.027750	0.736392
60.000000	4.786738	0.027545	0.737829
61.000000	4.755368	0.027343	0.739207
62.000000	4.724223	0.027143	0.740529
63.000000	4.693300	0.026946	0.741798
64.000000	4.662596	0.026751	0.743017
65.000000	4.632109	0.026558	0.744189
66.000000	4.601837	0.026368	0.745316
67.000000	4.571777	0.026179	0.746402
68.000000	4.541928	0.025993	0.747448
69.000000	4.512285	0.025808	0.748457
70.000000	4.482849	0.025626	0.749430
71.000000	4.453616	0.025445	0.750370
72.000000	4.424584	0.025266	0.751278
73.000000	4.395752	0.025089	0.752157
74.000000	4.367118	0.024913	0.753008
75.000000	4.338680	0.024739	0.753833
76.000000	4.310435	0.024567	0.754632
77.000000	4.282383	0.024396	0.755408
78.000000	4.254521	0.024227	0.756162

79.000000	4.226848	0.024059	0.756895
80.000000	4.199363	0.023893	0.757609
81.000000	4.172062	0.023729	0.758304
82.000000	4.144946	0.023565	0.758981
83.000000	4.118013	0.023403	0.759642
84.000000	4.091260	0.023243	0.760287
85.000000	4.064687	0.023084	0.760918
86.000000	4.038291	0.022926	0.761535
87.000000	4.012073	0.022769	0.762139
88.000000	3.986029	0.022614	0.762731
89.000000	3.960160	0.022459	0.763311
90.000000	3.934462	0.022306	0.763880
91.000000	3.908936	0.022155	0.764439
92.000000	3.883580	0.022004	0.764989
93.000000	3.858392	0.021855	0.765529
94.000000	3.833372	0.021707	0.766061
95.000000	3.808518	0.021559	0.766585
96.000000	3.783828	0.021413	0.767101
97.000000	3.759302	0.021268	0.767610
98.000000	3.734938	0.021125	0.768112
99.000000	3.710735	0.020982	0.768608
100.000000	3.686693	0.020840	0.769098
101.000000	3.662809	0.020699	0.769583
102.000000	3.639083	0.020560	0.770062
103.000000	3.615513	0.020421	0.770536
104.000000	3.592099	0.020284	0.771005
105.000000	3.568839	0.020147	0.771471
106.000000	3.545733	0.020011	0.771932
107.000000	3.522778	0.019877	0.772389
108.000000	3.499975	0.019743	0.772842
109.000000	3.477322	0.019610	0.773292
110.000000	3.454817	0.019478	0.773739
111.000000	3.432461	0.019347	0.774183
112.000000	3.410252	0.019217	0.774624
113.000000	3.388188	0.019088	0.775063
114.000000	3.366270	0.018960	0.775499
115.000000	3.344495	0.018833	0.775932
116.000000	3.322863	0.018707	0.776363
117.000000	3.301374	0.018581	0.776793
118.000000	3.280025	0.018457	0.777220
119.000000	3.258816	0.018333	0.777645
120.000000	3.237746	0.018210	0.778069

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.073443	0.000005
1.000000	0.071796	0.001019
2.000000	0.070233	0.001962
3.000000	0.068749	0.002839
4.000000	0.067341	0.003654
5.000000	0.066002	0.004411
6.000000	0.064729	0.005114

```
 7.000000       0.063518       0.005765
 8.000000       0.062364       0.006370
 9.000000       0.061265       0.006929
10.000000       0.060217       0.007447
11.000000       0.059217       0.007926
12.000000       0.058262       0.008369
13.000000       0.057349       0.008777
14.000000       0.056476       0.009154
15.000000       0.055640       0.009501
16.000000       0.054839       0.009819
17.000000       0.054071       0.010112
18.000000       0.053334       0.010380
19.000000       0.052626       0.010626
20.000000       0.051946       0.010850
21.000000       0.051292       0.011054
22.000000       0.050661       0.011240
23.000000       0.050054       0.011408
24.000000       0.049468       0.011560
25.000000       0.048902       0.011697
26.000000       0.048355       0.011819
27.000000       0.047826       0.011928
28.000000       0.047314       0.012025
29.000000       0.046818       0.012110
30.000000       0.046338       0.012185
31.000000       0.045871       0.012249
32.000000       0.045418       0.012304
33.000000       0.044977       0.012351
34.000000       0.044549       0.012389
35.000000       0.044131       0.012419
36.000000       0.043725       0.012443
37.000000       0.043328       0.012459
38.000000       0.042941       0.012470
39.000000       0.042563       0.012475
40.000000       0.042194       0.012474
41.000000       0.041833       0.012469
42.000000       0.041480       0.012459
43.000000       0.041134       0.012445
44.000000       0.040795       0.012426
45.000000       0.040462       0.012404
46.000000       0.040136       0.012379
47.000000       0.039816       0.012350
48.000000       0.039502       0.012319
49.000000       0.039193       0.012284
50.000000       0.038889       0.012247
51.000000       0.038590       0.012208
52.000000       0.038296       0.012167
53.000000       0.038007       0.012123
54.000000       0.037722       0.012078
55.000000       0.037441       0.012031
56.000000       0.037164       0.011983
57.000000       0.036890       0.011933
58.000000       0.036621       0.011882
59.000000       0.036355       0.011830
60.000000       0.036092       0.011776
61.000000       0.035833       0.011722
62.000000       0.035577       0.011667
```

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 63.000000       0.035324       0.011610
 64.000000       0.035074       0.011554
 65.000000       0.034826       0.011496
 66.000000       0.034582       0.011438
 67.000000       0.034340       0.011379
 68.000000       0.034100       0.011320
 69.000000       0.033863       0.011261
 70.000000       0.033629       0.011201
 71.000000       0.033397       0.011141
 72.000000       0.033167       0.011080
 73.000000       0.032939       0.011020
 74.000000       0.032714       0.010959
 75.000000       0.032490       0.010898
 76.000000       0.032269       0.010837
 77.000000       0.032049       0.010776
 78.000000       0.031832       0.010714
 79.000000       0.031616       0.010653
 80.000000       0.031403       0.010592
 81.000000       0.031191       0.010531
 82.000000       0.030981       0.010470
 83.000000       0.030773       0.010409
 84.000000       0.030566       0.010348
 85.000000       0.030361       0.010287
 86.000000       0.030158       0.010226
 87.000000       0.029956       0.010166
 88.000000       0.029756       0.010105
 89.000000       0.029558       0.010045
 90.000000       0.029361       0.009985
 91.000000       0.029165       0.009925
 92.000000       0.028971       0.009865
 93.000000       0.028779       0.009806
 94.000000       0.028588       0.009747
 95.000000       0.028398       0.009688
 96.000000       0.028210       0.009629
 97.000000       0.028023       0.009571
 98.000000       0.027838       0.009512
 99.000000       0.027654       0.009455
100.000000       0.027471       0.009397
101.000000       0.027290       0.009339
102.000000       0.027109       0.009282
103.000000       0.026931       0.009225
104.000000       0.026753       0.009169
105.000000       0.026577       0.009113
106.000000       0.026402       0.009056
107.000000       0.026228       0.009001
108.000000       0.026055       0.008945
109.000000       0.025884       0.008890
110.000000       0.025714       0.008835
111.000000       0.025545       0.008781
112.000000       0.025377       0.008727
113.000000       0.025210       0.008673
114.000000       0.025045       0.008619
115.000000       0.024880       0.008566
116.000000       0.024717       0.008513
117.000000       0.024555       0.008460
118.000000       0.024394       0.008407
```

119.000000	0.024234	0.008355
120.000000	0.024075	0.008303

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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 2018-2019


Version:       1.1
Date of this report:  20.04.2020 09:59

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 0.04    0       10000   False
c_LR    1       0.1     10000   False
M_0     8.042   0       10000   True
ExpFre  0.9     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     0.003   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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	7.510228	0.002148	0.000000
KOC_EQ	5.316813	0.004040	0.000000
f_NEQ	0.492963	0.014239	0.000000
k_des	0.043948	0.083957	0.305285
DT50_EQ	60.789838	0.001337	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	7.510228	7.506018	7.514438
KOC_EQ	5.316813	5.308895	5.324731
f_NEQ	0.492963	0.465055	0.520871
k_des	0.043948	-0.120608	0.208504
DT50_EQ	60.789838	60.787217	60.792458

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	2.968165
Weighted ME (Chi²)	1.926749
Coeff. of Det. (R²)	0.999152
Model efficiency	0.999046
Abs. deviation	1.893198
Quadr. deviation	0.318538
SRMSE	0.033055
STE	0.019601

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R^2)	0.995542	0.997449
Model efficiency	0.993716	0.997415
Abs. deviation	1.883815	0.009383
Quadr. deviation	0.318528	0.000009
SRMSE	0.023540	0.017809
STE	0.019644	0.013656

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R^2)	0.963599
Model efficiency	0.915856
Abs. deviation	0.493713
Quadr. deviation	0.019510
SRMSE	0.079789
STE	0.070507

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.680000	7.509718	0.170282	0.01695
0.000	7.670000	7.509718	0.160282	0.01700
1.000	7.700000	7.424945	0.275055	0.01687
1.000	7.660000	7.424945	0.235055	0.01704
3.000	7.320000	7.260342	0.059658	0.01866
3.000	7.340000	7.260342	0.079658	0.01856
7.000	6.990000	6.949707	0.040293	0.02047
7.000	6.990000	6.949707	0.040293	0.02047
14.000	6.380000	6.455126	-0.075126	0.02457
14.000	6.380000	6.455126	-0.075126	0.02457
30.000	5.410000	5.503793	-0.093793	0.03417
30.000	5.430000	5.503793	-0.073793	0.03392
58.000	4.010000	4.231419	-0.221419	0.06219
58.000	4.030000	4.231419	-0.201419	0.06157
120.000	2.430000	2.413718	0.016282	0.16935
120.000	2.480000	2.413718	0.066282	0.16259

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.060000	0.058561	0.001439	277.77778
0.000	0.058500	0.058561	-0.000061	292.20542
1.000	0.058000	0.057372	0.000628	297.26516
1.000	0.058000	0.057372	0.000628	297.26516
3.000	0.053600	0.055127	-0.001527	348.07307
3.000	0.053500	0.055127	-0.001627	349.37549
7.000	0.050700	0.051120	-0.000420	389.03089
7.000	0.050500	0.051120	-0.000620	392.11842
14.000	0.045400	0.045331	0.000069	485.16369
14.000	0.045500	0.045331	0.000169	483.03345

30.000	0.036400	0.035999	0.000401	754.73977
30.000	0.036200	0.035999	0.000201	763.10247
58.000	0.025500	0.026138	-0.000638	1537.87005
58.000	0.025900	0.026138	-0.000238	1490.73508
120.000	0.014700	0.014341	0.000359	4627.70142
120.000	0.014700	0.014341	0.000359	4627.70142

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	0.280000	0.282456	-0.002456	277.77778
0.000000	0.311111	0.282456	0.028655	292.20542
1.000000	0.327586	0.294263	0.033324	297.26516
1.000000	0.320690	0.294263	0.026427	297.26516
3.000000	0.365672	0.317103	0.048568	348.07307
3.000000	0.371963	0.317103	0.054859	349.37549
7.000000	0.378698	0.359590	0.019108	389.03089
7.000000	0.384158	0.359590	0.024568	392.11842
14.000000	0.405286	0.424075	-0.018789	485.16369
14.000000	0.402198	0.424075	-0.021877	483.03345
30.000000	0.486264	0.528973	-0.042709	754.73977
30.000000	0.500000	0.528973	-0.028973	763.10247
58.000000	0.572549	0.618959	-0.046410	1537.87005
58.000000	0.555985	0.618959	-0.062975	1490.73508
120.000000	0.653061	0.683167	-0.030106	4627.70142
120.000000	0.687075	0.683167	0.003908	4627.70142

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	7.509718	0.058561	0.282456
1.000000	7.424945	0.057372	0.294263
2.000000	7.341841	0.056228	0.305813
3.000000	7.260342	0.055127	0.317103
4.000000	7.180390	0.054067	0.328133
5.000000	7.101928	0.053046	0.338901
6.000000	7.024902	0.052063	0.349407
7.000000	6.949261	0.051114	0.359650
8.000000	6.874955	0.050199	0.369632
9.000000	6.801939	0.049316	0.379354
10.000000	6.730169	0.048463	0.388816
11.000000	6.659602	0.047639	0.398022
12.000000	6.590198	0.046842	0.406973
13.000000	6.521920	0.046072	0.415673
14.000000	6.454730	0.045327	0.424124
15.000000	6.388594	0.044606	0.432331
16.000000	6.323479	0.043907	0.440295
17.000000	6.259353	0.043230	0.448023
18.000000	6.196187	0.042573	0.455517
19.000000	6.133952	0.041936	0.462782
20.000000	6.072620	0.041318	0.469823
21.000000	6.012166	0.040718	0.476644
22.000000	5.952564	0.040134	0.483251
23.000000	5.893791	0.039567	0.489647
24.000000	5.835824	0.039016	0.495839
25.000000	5.778641	0.038480	0.501831
26.000000	5.722221	0.037957	0.507628

```
27.000000       5.666545       0.037449       0.513236
28.000000       5.611594       0.036953       0.518659
29.000000       5.557349       0.036470       0.523903
30.000000       5.503793       0.035999       0.528973
31.000000       5.450909       0.035539       0.533874
32.000000       5.398682       0.035090       0.538611
33.000000       5.347096       0.034652       0.543189
34.000000       5.296136       0.034223       0.547613
35.000000       5.245789       0.033805       0.551888
36.000000       5.196040       0.033395       0.556019
37.000000       5.146878       0.032994       0.560010
38.000000       5.098289       0.032602       0.563867
39.000000       5.050262       0.032219       0.567593
40.000000       5.002785       0.031842       0.571193
41.000000       4.955846       0.031474       0.574672
42.000000       4.909437       0.031113       0.578033
43.000000       4.863545       0.030759       0.581282
44.000000       4.818162       0.030411       0.584421
45.000000       4.773277       0.030070       0.587456
46.000000       4.728883       0.029736       0.590389
47.000000       4.684969       0.029407       0.593225
48.000000       4.641528       0.029084       0.595968
49.000000       4.598550       0.028767       0.598620
50.000000       4.556030       0.028456       0.601185
51.000000       4.513957       0.028149       0.603667
52.000000       4.472326       0.027848       0.606068
53.000000       4.431129       0.027552       0.608393
54.000000       4.390359       0.027260       0.610643
55.000000       4.350010       0.026973       0.612822
56.000000       4.310074       0.026690       0.614932
57.000000       4.270546       0.026412       0.616977
58.000000       4.231419       0.026138       0.618959
59.000000       4.192688       0.025868       0.620881
60.000000       4.154347       0.025602       0.622744
61.000000       4.116390       0.025340       0.624552
62.000000       4.078812       0.025082       0.626306
63.000000       4.041607       0.024827       0.628009
64.000000       4.004771       0.024576       0.629663
65.000000       3.968298       0.024328       0.631270
66.000000       3.932184       0.024083       0.632831
67.000000       3.896423       0.023842       0.634350
68.000000       3.861012       0.023604       0.635827
69.000000       3.825945       0.023369       0.637264
70.000000       3.791218       0.023137       0.638663
71.000000       3.756828       0.022908       0.640026
72.000000       3.722769       0.022682       0.641354
73.000000       3.689038       0.022459       0.642648
74.000000       3.655631       0.022239       0.643911
75.000000       3.622543       0.022021       0.645143
76.000000       3.589772       0.021806       0.646345
77.000000       3.557313       0.021593       0.647520
78.000000       3.525162       0.021383       0.648668
79.000000       3.493316       0.021175       0.649790
80.000000       3.461772       0.020970       0.650887
81.000000       3.430526       0.020768       0.651961
82.000000       3.399575       0.020567       0.653013
```

83.000000	3.368915	0.020369	0.654043
84.000000	3.338544	0.020173	0.655053
85.000000	3.308457	0.019979	0.656043
86.000000	3.278652	0.019788	0.657014
87.000000	3.249126	0.019598	0.657967
88.000000	3.219876	0.019411	0.658903
89.000000	3.190898	0.019225	0.659823
90.000000	3.162191	0.019042	0.660727
91.000000	3.133750	0.018861	0.661616
92.000000	3.105574	0.018681	0.662491
93.000000	3.077659	0.018504	0.663352
94.000000	3.050003	0.018328	0.664200
95.000000	3.022603	0.018154	0.665036
96.000000	2.995457	0.017982	0.665859
97.000000	2.968561	0.017812	0.666672
98.000000	2.941913	0.017644	0.667473
99.000000	2.915511	0.017477	0.668264
100.000000	2.889353	0.017312	0.669046
101.000000	2.863435	0.017149	0.669817
102.000000	2.837756	0.016988	0.670580
103.000000	2.812312	0.016828	0.671335
104.000000	2.787103	0.016669	0.672081
105.000000	2.762124	0.016513	0.672819
106.000000	2.737375	0.016358	0.673550
107.000000	2.712852	0.016204	0.674273
108.000000	2.688554	0.016052	0.674990
109.000000	2.664478	0.015902	0.675701
110.000000	2.640623	0.015753	0.676405
111.000000	2.616985	0.015605	0.677103
112.000000	2.593564	0.015459	0.677796
113.000000	2.570356	0.015314	0.678484
114.000000	2.547360	0.015171	0.679166
115.000000	2.524573	0.015029	0.679844
116.000000	2.501995	0.014889	0.680517
117.000000	2.479622	0.014750	0.681185
118.000000	2.457453	0.014612	0.681850
119.000000	2.435485	0.014476	0.682510
120.000000	2.413718	0.014341	0.683167

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.075102	0.000004
1.000000	0.073610	0.000648
2.000000	0.072175	0.001252
3.000000	0.070793	0.001819
4.000000	0.069461	0.002350
5.000000	0.068179	0.002848
6.000000	0.066942	0.003314
7.000000	0.065749	0.003751
8.000000	0.064598	0.004158
9.000000	0.063487	0.004539
10.000000	0.062413	0.004895

```
11.000000       0.061375       0.005227
12.000000       0.060372       0.005536
13.000000       0.059402       0.005823
14.000000       0.058462       0.006091
15.000000       0.057552       0.006339
16.000000       0.056671       0.006569
17.000000       0.055816       0.006782
18.000000       0.054987       0.006979
19.000000       0.054183       0.007161
20.000000       0.053402       0.007328
21.000000       0.052644       0.007482
22.000000       0.051907       0.007623
23.000000       0.051190       0.007752
24.000000       0.050493       0.007869
25.000000       0.049814       0.007976
26.000000       0.049154       0.008072
27.000000       0.048510       0.008159
28.000000       0.047883       0.008237
29.000000       0.047271       0.008306
30.000000       0.046674       0.008368
31.000000       0.046091       0.008421
32.000000       0.045522       0.008468
33.000000       0.044966       0.008508
34.000000       0.044423       0.008541
35.000000       0.043892       0.008569
36.000000       0.043373       0.008591
37.000000       0.042864       0.008608
38.000000       0.042367       0.008619
39.000000       0.041879       0.008626
40.000000       0.041402       0.008629
41.000000       0.040934       0.008628
42.000000       0.040475       0.008622
43.000000       0.040024       0.008614
44.000000       0.039583       0.008601
45.000000       0.039149       0.008586
46.000000       0.038724       0.008568
47.000000       0.038306       0.008546
48.000000       0.037895       0.008523
49.000000       0.037491       0.008496
50.000000       0.037095       0.008468
51.000000       0.036705       0.008437
52.000000       0.036321       0.008405
53.000000       0.035943       0.008370
54.000000       0.035572       0.008334
55.000000       0.035206       0.008297
56.000000       0.034845       0.008257
57.000000       0.034491       0.008217
58.000000       0.034141       0.008175
59.000000       0.033797       0.008132
60.000000       0.033457       0.008088
61.000000       0.033123       0.008043
62.000000       0.032793       0.007997
63.000000       0.032468       0.007950
64.000000       0.032147       0.007903
65.000000       0.031830       0.007855
66.000000       0.031518       0.007806
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 67.000000       0.031210       0.007756
 68.000000       0.030905       0.007707
 69.000000       0.030605       0.007656
 70.000000       0.030309       0.007605
 71.000000       0.030016       0.007554
 72.000000       0.029726       0.007503
 73.000000       0.029441       0.007451
 74.000000       0.029159       0.007399
 75.000000       0.028880       0.007347
 76.000000       0.028604       0.007295
 77.000000       0.028332       0.007243
 78.000000       0.028063       0.007190
 79.000000       0.027797       0.007138
 80.000000       0.027534       0.007085
 81.000000       0.027274       0.007033
 82.000000       0.027017       0.006980
 83.000000       0.026763       0.006928
 84.000000       0.026512       0.006875
 85.000000       0.026263       0.006823
 86.000000       0.026017       0.006771
 87.000000       0.025774       0.006719
 88.000000       0.025533       0.006667
 89.000000       0.025295       0.006615
 90.000000       0.025060       0.006563
 91.000000       0.024827       0.006512
 92.000000       0.024597       0.006461
 93.000000       0.024368       0.006410
 94.000000       0.024143       0.006359
 95.000000       0.023919       0.006308
 96.000000       0.023698       0.006258
 97.000000       0.023479       0.006208
 98.000000       0.023263       0.006158
 99.000000       0.023048       0.006108
100.000000       0.022836       0.006059
101.000000       0.022626       0.006010
102.000000       0.022418       0.005961
103.000000       0.022212       0.005912
104.000000       0.022008       0.005864
105.000000       0.021806       0.005816
106.000000       0.021606       0.005769
107.000000       0.021408       0.005721
108.000000       0.021212       0.005674
109.000000       0.021018       0.005628
110.000000       0.020826       0.005581
111.000000       0.020636       0.005535
112.000000       0.020448       0.005489
113.000000       0.020261       0.005444
114.000000       0.020076       0.005399
115.000000       0.019893       0.005354
116.000000       0.019712       0.005309
117.000000       0.019532       0.005265
118.000000       0.019354       0.005221
119.000000       0.019178       0.005178
120.000000       0.019004       0.005134
```

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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 2018-2019

Version: 1.1
Date of this report: 20.04.2020 10:04

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	0.049
3	7.2	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	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	0.9	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	0.003	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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	7.191008	0.004024	0.000000
KOC_EQ	13.384028	0.003007	0.000000
f_NEQ	0.512024	0.020430	0.000000
k_des	0.048690	0.104078	0.319419
DT50_EQ	142.774780	0.000296	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	7.191008	7.183121	7.198895
KOC_EQ	13.384028	13.378135	13.389921
f_NEQ	0.512024	0.471981	0.552068
k_des	0.048690	-0.155304	0.252684
DT50_EQ	142.774780	142.774199	142.775361

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

	Complete Data Set
No obs.	32

No act. param. 5
Deg. of Freedom 11
Model error (Chi²) 3.854075
Weighted ME (Chi²) 2.164434
Coeff. of Det. (R²) 0.997955
Model efficiency 0.997934
Abs. deviation 2.957866
Quadr. deviation 0.713253
SRMSE 0.045858
STE 0.028392

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R²)	0.951376	0.994979
Model efficiency	0.949685	0.994975
Abs. deviation	2.949691	0.008175
Quadr. deviation	0.713247	0.000006
SRMSE	0.032623	0.015859
STE	0.028486	0.013012

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R²)	0.870200
Model efficiency	0.848557
Abs. deviation	0.886197
Quadr. deviation	0.067631
SRMSE	0.095085
STE	0.081004

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.440000	7.190826	0.249174	0.01807
0.000	7.510000	7.190826	0.319174	0.01773
1.000	7.210000	7.156399	0.053601	0.01924
1.000	7.330000	7.156399	0.173601	0.01861
3.000	7.200000	7.088912	0.111088	0.01929
3.000	7.260000	7.088912	0.171088	0.01897
7.000	7.160000	6.959929	0.200071	0.01951
7.000	6.980000	6.959929	0.020071	0.02053
14.000	6.390000	6.750679	-0.360679	0.02449
14.000	6.720000	6.750679	-0.030679	0.02214
30.000	6.030000	6.323947	-0.293947	0.02750
30.000	6.010000	6.323947	-0.313947	0.02769
58.000	5.430000	5.677136	-0.247136	0.03392
58.000	5.580000	5.677136	-0.097136	0.03212
120.000	4.640000	4.495850	0.144150	0.04645
120.000	4.660000	4.495850	0.164150	0.04605

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.049400	0.048865	0.000535	409.77561
0.000	0.049500	0.048865	0.000635	408.12162
1.000	0.048200	0.047999	0.000201	430.43336
1.000	0.049000	0.047999	0.001001	416.49313
3.000	0.045300	0.046389	-0.001089	487.30806
3.000	0.045700	0.046389	-0.000689	478.81484
7.000	0.043400	0.043619	-0.000219	530.90955
7.000	0.042500	0.043619	-0.001119	553.63322
14.000	0.039500	0.039904	-0.000404	640.92293
14.000	0.039900	0.039904	-0.000004	628.13676
30.000	0.035200	0.034609	0.000591	807.07645
30.000	0.035500	0.034609	0.000891	793.49335
58.000	0.029300	0.029669	-0.000369	1164.83593
58.000	0.029900	0.029669	0.000231	1118.55572
120.000	0.022900	0.023013	-0.000113	1906.90490
120.000	0.023100	0.023013	0.000087	1874.02785

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	0.505073	0.470609	0.034464	409.77561
0.000000	0.516172	0.470609	0.045563	408.12162
1.000000	0.494851	0.489986	0.004865	430.43336
1.000000	0.494918	0.489986	0.004933	416.49313
3.000000	0.588404	0.527197	0.061207	487.30806
3.000000	0.587621	0.527197	0.060424	478.81484
7.000000	0.648770	0.594672	0.054098	530.90955
7.000000	0.641353	0.594672	0.046681	553.63322
14.000000	0.616722	0.690773	-0.074052	640.92293
14.000000	0.683211	0.690773	-0.007563	628.13676
30.000000	0.712068	0.826267	-0.114199	807.07645
30.000000	0.691958	0.826267	-0.134310	793.49335
58.000000	0.852242	0.912511	-0.060269	1164.83593
58.000000	0.865221	0.912511	-0.047290	1118.55572
120.000000	1.025201	0.952618	0.072583	1906.90490
120.000000	1.016316	0.952618	0.063698	1874.02785

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	7.190826	0.048865	0.470609
1.000000	7.156220	0.047995	0.490086
2.000000	7.122201	0.047169	0.508981
3.000000	7.088739	0.046385	0.527291
4.000000	7.055806	0.045640	0.545014
5.000000	7.023376	0.044932	0.562150
6.000000	6.991425	0.044259	0.578701
7.000000	6.959929	0.043619	0.594672
8.000000	6.928867	0.043009	0.610067
9.000000	6.898218	0.042428	0.624894
10.000000	6.867962	0.041875	0.639161
11.000000	6.838082	0.041347	0.652877
12.000000	6.808561	0.040843	0.666054
13.000000	6.779381	0.040362	0.678703

14.000000	6.750530	0.039902	0.690835
15.000000	6.721991	0.039462	0.702464
16.000000	6.693751	0.039041	0.713604
17.000000	6.665799	0.038637	0.724269
18.000000	6.638121	0.038251	0.734472
19.000000	6.610708	0.037880	0.744229
20.000000	6.583548	0.037524	0.753554
21.000000	6.556631	0.037181	0.762462
22.000000	6.529948	0.036852	0.770968
23.000000	6.503490	0.036536	0.779086
24.000000	6.477249	0.036231	0.786831
25.000000	6.451216	0.035936	0.794218
26.000000	6.425386	0.035653	0.801262
27.000000	6.399750	0.035379	0.807974
28.000000	6.374303	0.035114	0.814371
29.000000	6.349037	0.034858	0.820464
30.000000	6.323947	0.034609	0.826267
31.000000	6.299028	0.034369	0.831794
32.000000	6.274274	0.034136	0.837056
33.000000	6.249681	0.033910	0.842065
34.000000	6.225244	0.033690	0.846833
35.000000	6.200958	0.033476	0.851371
36.000000	6.176820	0.033269	0.855690
37.000000	6.152825	0.033066	0.859800
38.000000	6.128970	0.032869	0.863712
39.000000	6.105251	0.032676	0.867435
40.000000	6.081666	0.032489	0.870978
41.000000	6.058210	0.032305	0.874351
42.000000	6.034881	0.032126	0.877561
43.000000	6.011677	0.031950	0.880617
44.000000	5.988595	0.031778	0.883527
45.000000	5.965631	0.031610	0.886299
46.000000	5.942784	0.031445	0.888938
47.000000	5.920052	0.031283	0.891453
48.000000	5.897432	0.031124	0.893849
49.000000	5.874923	0.030968	0.896133
50.000000	5.852522	0.030815	0.898310
51.000000	5.830228	0.030664	0.900387
52.000000	5.808039	0.030515	0.902368
53.000000	5.785954	0.030369	0.904259
54.000000	5.763970	0.030225	0.906065
55.000000	5.742086	0.030083	0.907789
56.000000	5.720302	0.029943	0.909437
57.000000	5.698614	0.029805	0.911012
58.000000	5.677024	0.029669	0.912519
59.000000	5.655528	0.029534	0.913960
60.000000	5.634126	0.029401	0.915341
61.000000	5.612817	0.029270	0.916663
62.000000	5.591600	0.029140	0.917930
63.000000	5.570474	0.029011	0.919146
64.000000	5.549437	0.028884	0.920312
65.000000	5.528490	0.028758	0.921433
66.000000	5.507630	0.028634	0.922509
67.000000	5.486857	0.028510	0.923544
68.000000	5.466171	0.028388	0.924540
69.000000	5.445570	0.028267	0.925499

70.000000	5.425054	0.028147	0.926423
71.000000	5.404621	0.028028	0.927315
72.000000	5.384273	0.027910	0.928175
73.000000	5.364007	0.027793	0.929006
74.000000	5.343822	0.027677	0.929809
75.000000	5.323720	0.027562	0.930585
76.000000	5.303698	0.027448	0.931338
77.000000	5.283756	0.027334	0.932066
78.000000	5.263894	0.027221	0.932773
79.000000	5.244110	0.027109	0.933459
80.000000	5.224406	0.026998	0.934125
81.000000	5.204779	0.026888	0.934773
82.000000	5.185230	0.026778	0.935404
83.000000	5.165758	0.026669	0.936017
84.000000	5.146363	0.026561	0.936616
85.000000	5.127043	0.026453	0.937199
86.000000	5.107799	0.026346	0.937769
87.000000	5.088631	0.026240	0.938325
88.000000	5.069537	0.026134	0.938870
89.000000	5.050518	0.026029	0.939402
90.000000	5.031572	0.025924	0.939924
91.000000	5.012700	0.025820	0.940435
92.000000	4.993901	0.025717	0.940937
93.000000	4.975175	0.025614	0.941429
94.000000	4.956522	0.025511	0.941913
95.000000	4.937940	0.025409	0.942388
96.000000	4.919430	0.025308	0.942856
97.000000	4.900992	0.025207	0.943317
98.000000	4.882624	0.025107	0.943770
99.000000	4.864327	0.025007	0.944217
100.000000	4.846100	0.024908	0.944658
101.000000	4.827944	0.024809	0.945094
102.000000	4.809857	0.024710	0.945523
103.000000	4.791839	0.024613	0.945948
104.000000	4.773890	0.024515	0.946368
105.000000	4.756010	0.024418	0.946783
106.000000	4.738198	0.024321	0.947195
107.000000	4.720455	0.024225	0.947602
108.000000	4.702779	0.024130	0.948005
109.000000	4.685171	0.024034	0.948405
110.000000	4.667629	0.023939	0.948801
111.000000	4.650155	0.023845	0.949194
112.000000	4.632747	0.023751	0.949585
113.000000	4.615406	0.023657	0.949972
114.000000	4.598131	0.023564	0.950357
115.000000	4.580921	0.023471	0.950739
116.000000	4.563777	0.023379	0.951119
117.000000	4.546698	0.023287	0.951497
118.000000	4.529684	0.023195	0.951872
119.000000	4.512735	0.023104	0.952246
120.000000	4.495850	0.023013	0.952618

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.071910	0.000005
1.000000	0.070670	0.000899
2.000000	0.069492	0.001736
3.000000	0.068374	0.002519
4.000000	0.067311	0.003252
5.000000	0.066300	0.003938
6.000000	0.065339	0.004580
7.000000	0.064424	0.005180
8.000000	0.063552	0.005741
9.000000	0.062722	0.006265
10.000000	0.061930	0.006754
11.000000	0.061174	0.007211
12.000000	0.060452	0.007637
13.000000	0.059763	0.008034
14.000000	0.059104	0.008405
15.000000	0.058473	0.008750
16.000000	0.057869	0.009071
17.000000	0.057291	0.009370
18.000000	0.056736	0.009648
19.000000	0.056204	0.009906
20.000000	0.055692	0.010146
21.000000	0.055201	0.010368
22.000000	0.054728	0.010574
23.000000	0.054273	0.010764
24.000000	0.053835	0.010940
25.000000	0.053412	0.011102
26.000000	0.053004	0.011252
27.000000	0.052610	0.011390
28.000000	0.052229	0.011516
29.000000	0.051860	0.011632
30.000000	0.051503	0.011738
31.000000	0.051157	0.011835
32.000000	0.050822	0.011923
33.000000	0.050496	0.012003
34.000000	0.050179	0.012075
35.000000	0.049872	0.012140
36.000000	0.049572	0.012198
37.000000	0.049280	0.012250
38.000000	0.048996	0.012295
39.000000	0.048718	0.012336
40.000000	0.048447	0.012371
41.000000	0.048183	0.012401
42.000000	0.047924	0.012426
43.000000	0.047671	0.012447
44.000000	0.047423	0.012464
45.000000	0.047180	0.012478
46.000000	0.046942	0.012487
47.000000	0.046708	0.012494
48.000000	0.046478	0.012497
49.000000	0.046253	0.012497
50.000000	0.046031	0.012495
51.000000	0.045813	0.012490
52.000000	0.045599	0.012483
53.000000	0.045387	0.012473

```
 54.000000       0.045179       0.012462
 55.000000       0.044974       0.012448
 56.000000       0.044772       0.012432
 57.000000       0.044572       0.012415
 58.000000       0.044375       0.012396
 59.000000       0.044180       0.012376
 60.000000       0.043988       0.012354
 61.000000       0.043798       0.012331
 62.000000       0.043610       0.012307
 63.000000       0.043424       0.012282
 64.000000       0.043240       0.012255
 65.000000       0.043058       0.012228
 66.000000       0.042878       0.012200
 67.000000       0.042699       0.012170
 68.000000       0.042522       0.012141
 69.000000       0.042347       0.012110
 70.000000       0.042173       0.012079
 71.000000       0.042001       0.012047
 72.000000       0.041830       0.012014
 73.000000       0.041660       0.011981
 74.000000       0.041492       0.011947
 75.000000       0.041325       0.011913
 76.000000       0.041159       0.011879
 77.000000       0.040995       0.011844
 78.000000       0.040831       0.011809
 79.000000       0.040669       0.011773
 80.000000       0.040508       0.011737
 81.000000       0.040347       0.011701
 82.000000       0.040188       0.011665
 83.000000       0.040030       0.011628
 84.000000       0.039873       0.011592
 85.000000       0.039717       0.011555
 86.000000       0.039561       0.011518
 87.000000       0.039407       0.011480
 88.000000       0.039253       0.011443
 89.000000       0.039100       0.011406
 90.000000       0.038949       0.011368
 91.000000       0.038797       0.011330
 92.000000       0.038647       0.011293
 93.000000       0.038498       0.011255
 94.000000       0.038349       0.011217
 95.000000       0.038201       0.011179
 96.000000       0.038054       0.011141
 97.000000       0.037907       0.011104
 98.000000       0.037761       0.011066
 99.000000       0.037616       0.011028
100.000000       0.037472       0.010990
101.000000       0.037328       0.010952
102.000000       0.037185       0.010915
103.000000       0.037042       0.010877
104.000000       0.036900       0.010839
105.000000       0.036759       0.010802
106.000000       0.036619       0.010764
107.000000       0.036479       0.010726
108.000000       0.036340       0.010689
109.000000       0.036201       0.010652
```

110.000000	0.036063	0.010614
111.000000	0.035925	0.010577
112.000000	0.035788	0.010540
113.000000	0.035652	0.010503
114.000000	0.035516	0.010466
115.000000	0.035381	0.010429
116.000000	0.035247	0.010392
117.000000	0.035113	0.010355
118.000000	0.034979	0.010318
119.000000	0.034846	0.010282
120.000000	0.034714	0.010245

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  20.04.2020 10:22

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    0.036
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      5.4     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  0.94    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     0.003   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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	6.910690	0.007009	0.000000
KOC_EQ	14.968404	0.007805	0.000000
f_NEQ	0.441788	0.063949	0.000000
k_des	0.073528	0.191108	0.352051
DT50_EQ	92.572166	0.001590	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	6.910690	6.896952	6.924429
KOC_EQ	14.968404	14.953107	14.983701
f_NEQ	0.441788	0.316447	0.567128
k_des	0.073528	-0.301043	0.448099
DT50_EQ	92.572166	92.569050	92.575282

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	7.961948
Weighted ME (Chi²)	4.958300
Coeff. of Det. (R²)	0.992234
Model efficiency	0.991633
Abs. deviation	5.312120
Quadr. deviation	2.629004
SRMSE	0.094686
STE	0.054838

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R^2)	0.912973	0.993585
Model efficiency	0.902123	0.993521
Abs. deviation	5.303677	0.008443
Quadr. deviation	2.628996	0.000008
SRMSE	0.067293	0.022804
STE	0.055029	0.017259

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R^2)	0.579965
Model efficiency	0.475021
Abs. deviation	1.970716
Quadr. deviation	0.411447
SRMSE	0.156902
STE	0.120513

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	7.380000	6.910494	0.469506	0.01836
0.000	7.370000	6.910494	0.459506	0.01841
1.000	7.360000	6.859503	0.500497	0.01846
1.000	7.290000	6.859503	0.430497	0.01882
3.000	6.960000	6.761846	0.198154	0.02064
3.000	6.910000	6.761846	0.148154	0.02094
7.000	6.760000	6.579921	0.180079	0.02188
7.000	6.740000	6.579921	0.160079	0.02201
14.000	6.350000	6.293524	0.056476	0.02480
14.000	6.280000	6.293524	-0.013524	0.02536
30.000	5.400000	5.726682	-0.326682	0.03429
30.000	5.390000	5.726682	-0.336682	0.03442
58.000	4.670000	4.886625	-0.216625	0.04585
58.000	3.850000	4.886625	-1.036625	0.06747
120.000	3.820000	3.449705	0.370295	0.06853
120.000	3.850000	3.449705	0.400295	0.06747

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.041700	0.040890	0.000810	575.07950
0.000	0.041900	0.040890	0.001010	569.60259
1.000	0.040100	0.039692	0.000408	621.88668
1.000	0.039900	0.039692	0.000208	628.13676
3.000	0.036000	0.037579	-0.001579	771.60494
3.000	0.036100	0.037579	-0.001479	767.33604
7.000	0.034100	0.034248	-0.000148	859.98572
7.000	0.033900	0.034248	-0.000348	870.16298
14.000	0.030200	0.030355	-0.000155	1096.44314
14.000	0.030500	0.030355	0.000145	1074.97984

30.000	0.026300	0.025699	0.000601	1445.73436
30.000	0.025700	0.025699	0.000001	1514.02746
58.000	0.020900	0.021389	-0.000489	2289.32488
58.000	0.021200	0.021389	-0.000189	2224.99110
120.000	0.015300	0.014915	0.000385	4271.86125
120.000	0.015400	0.014915	0.000485	4216.56266

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	0.768784	0.689068	0.079716	575.07950
0.000000	0.757950	0.689068	0.068882	569.60259
1.000000	0.834411	0.727252	0.107159	621.88668
1.000000	0.826068	0.727252	0.098815	628.13676
3.000000	0.932333	0.798402	0.133931	771.60494
3.000000	0.913127	0.798402	0.114725	767.33604
7.000000	0.981405	0.920298	0.061107	859.98572
7.000000	0.987201	0.920298	0.066903	870.16298
14.000000	1.101649	1.072353	0.029296	1096.44314
14.000000	1.058016	1.072353	-0.014337	1074.97984
30.000000	1.052232	1.227421	-0.175189	1445.73436
30.000000	1.096276	1.227421	-0.131145	1514.02746
58.000000	1.233450	1.283668	-0.050218	2289.32488
58.000000	0.815038	1.283668	-0.468630	2224.99110
120.000000	1.495732	1.312035	0.183697	4271.86125
120.000000	1.499000	1.312035	0.186965	4216.56266

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	6.910494	0.040890	0.689068
1.000000	6.859503	0.039692	0.727252
2.000000	6.809931	0.038590	0.763750
3.000000	6.761666	0.037576	0.798531
4.000000	6.714605	0.036641	0.831579
5.000000	6.668654	0.035779	0.862894
6.000000	6.623731	0.034982	0.892493
7.000000	6.579756	0.034245	0.920400
8.000000	6.536661	0.033563	0.946653
9.000000	6.494382	0.032929	0.971298
10.000000	6.452861	0.032340	0.994387
11.000000	6.412046	0.031791	1.015980
12.000000	6.371888	0.031279	1.036138
13.000000	6.332345	0.030801	1.054928
14.000000	6.293378	0.030353	1.072417
15.000000	6.254949	0.029933	1.088674
16.000000	6.217027	0.029539	1.103769
17.000000	6.179581	0.029167	1.117769
18.000000	6.142585	0.028816	1.130741
19.000000	6.106014	0.028484	1.142750
20.000000	6.069845	0.028169	1.153859
21.000000	6.034058	0.027870	1.164129
22.000000	5.998635	0.027585	1.173618
23.000000	5.963558	0.027314	1.182381
24.000000	5.928811	0.027055	1.190471
25.000000	5.894381	0.026806	1.197936
26.000000	5.860254	0.026568	1.204825

```
27.000000       5.826418       0.026339       1.211179
28.000000       5.792864       0.026118       1.217042
29.000000       5.759580       0.025904       1.222450
30.000000       5.726558       0.025698       1.227439
31.000000       5.693789       0.025498       1.232044
32.000000       5.661265       0.025305       1.236294
33.000000       5.628980       0.025116       1.240218
34.000000       5.596928       0.024933       1.243843
35.000000       5.565101       0.024754       1.247194
36.000000       5.533495       0.024580       1.250293
37.000000       5.502104       0.024409       1.253160
38.000000       5.470924       0.024242       1.255815
39.000000       5.439951       0.024079       1.258277
40.000000       5.409180       0.023918       1.260560
41.000000       5.378608       0.023761       1.262681
42.000000       5.348231       0.023606       1.264653
43.000000       5.318046       0.023454       1.266488
44.000000       5.288050       0.023304       1.268199
45.000000       5.258240       0.023156       1.269795
46.000000       5.228613       0.023011       1.271287
47.000000       5.199167       0.022867       1.272684
48.000000       5.169900       0.022725       1.273993
49.000000       5.140810       0.022585       1.275223
50.000000       5.111894       0.022447       1.276380
51.000000       5.083150       0.022310       1.277470
52.000000       5.054577       0.022175       1.278500
53.000000       5.026172       0.022041       1.279474
54.000000       4.997935       0.021908       1.280398
55.000000       4.969863       0.021776       1.281275
56.000000       4.941955       0.021646       1.282110
57.000000       4.914209       0.021517       1.282907
58.000000       4.886625       0.021389       1.283668
59.000000       4.859200       0.021262       1.284397
60.000000       4.831933       0.021137       1.285097
61.000000       4.804824       0.021012       1.285770
62.000000       4.777870       0.020888       1.286418
63.000000       4.751072       0.020765       1.287045
64.000000       4.724426       0.020643       1.287651
65.000000       4.697934       0.020522       1.288238
66.000000       4.671592       0.020402       1.288809
67.000000       4.645401       0.020283       1.289364
68.000000       4.619359       0.020164       1.289905
69.000000       4.593465       0.020047       1.290433
70.000000       4.567719       0.019930       1.290949
71.000000       4.542118       0.019814       1.291455
72.000000       4.516663       0.019698       1.291951
73.000000       4.491353       0.019584       1.292439
74.000000       4.466185       0.019470       1.292918
75.000000       4.441161       0.019357       1.293389
76.000000       4.416278       0.019245       1.293855
77.000000       4.391536       0.019133       1.294314
78.000000       4.366933       0.019022       1.294767
79.000000       4.342470       0.018912       1.295215
80.000000       4.318145       0.018802       1.295659
81.000000       4.293958       0.018693       1.296099
82.000000       4.269906       0.018585       1.296534
```

83.000000	4.245991	0.018478	1.296967
84.000000	4.222211	0.018371	1.297396
85.000000	4.198564	0.018264	1.297822
86.000000	4.175051	0.018159	1.298246
87.000000	4.151671	0.018054	1.298667
88.000000	4.128422	0.017949	1.299086
89.000000	4.105305	0.017846	1.299503
90.000000	4.082318	0.017743	1.299918
91.000000	4.059460	0.017640	1.300332
92.000000	4.036731	0.017538	1.300744
93.000000	4.014129	0.017437	1.301155
94.000000	3.991656	0.017336	1.301565
95.000000	3.969308	0.017236	1.301974
96.000000	3.947087	0.017136	1.302382
97.000000	3.924990	0.017037	1.302788
98.000000	3.903018	0.016939	1.303195
99.000000	3.881170	0.016841	1.303600
100.000000	3.859444	0.016744	1.304005
101.000000	3.837841	0.016647	1.304409
102.000000	3.816359	0.016551	1.304812
103.000000	3.794999	0.016456	1.305216
104.000000	3.773758	0.016361	1.305618
105.000000	3.752637	0.016267	1.306021
106.000000	3.731634	0.016173	1.306423
107.000000	3.710750	0.016079	1.306825
108.000000	3.689983	0.015987	1.307226
109.000000	3.669333	0.015894	1.307627
110.000000	3.648800	0.015803	1.308029
111.000000	3.628381	0.015712	1.308430
112.000000	3.608078	0.015621	1.308831
113.000000	3.587888	0.015531	1.309231
114.000000	3.567812	0.015441	1.309632
115.000000	3.547849	0.015352	1.310033
116.000000	3.527998	0.015264	1.310433
117.000000	3.508259	0.015176	1.310834
118.000000	3.488631	0.015088	1.311234
119.000000	3.469113	0.015001	1.311635
120.000000	3.449705	0.014915	1.312035

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.069107	0.000006
1.000000	0.067130	0.001472
2.000000	0.065312	0.002794
3.000000	0.063637	0.003986
4.000000	0.062093	0.005059
5.000000	0.060667	0.006025
6.000000	0.059349	0.006893
7.000000	0.058130	0.007672
8.000000	0.056999	0.008372
9.000000	0.055949	0.008999
10.000000	0.054972	0.009560

```
11.000000       0.054062       0.010061
12.000000       0.053214       0.010508
13.000000       0.052420       0.010906
14.000000       0.051677       0.011260
15.000000       0.050979       0.011573
16.000000       0.050323       0.011850
17.000000       0.049705       0.012093
18.000000       0.049122       0.012306
19.000000       0.048569       0.012493
20.000000       0.048046       0.012654
21.000000       0.047549       0.012794
22.000000       0.047075       0.012913
23.000000       0.046624       0.013014
24.000000       0.046192       0.013098
25.000000       0.045778       0.013167
26.000000       0.045381       0.013223
27.000000       0.044999       0.013266
28.000000       0.044631       0.013299
29.000000       0.044276       0.013321
30.000000       0.043932       0.013335
31.000000       0.043599       0.013340
32.000000       0.043276       0.013338
33.000000       0.042962       0.013329
34.000000       0.042656       0.013315
35.000000       0.042358       0.013294
36.000000       0.042067       0.013269
37.000000       0.041782       0.013240
38.000000       0.041503       0.013207
39.000000       0.041230       0.013170
40.000000       0.040963       0.013130
41.000000       0.040700       0.013087
42.000000       0.040441       0.013042
43.000000       0.040187       0.012995
44.000000       0.039936       0.012945
45.000000       0.039690       0.012894
46.000000       0.039446       0.012841
47.000000       0.039206       0.012786
48.000000       0.038969       0.012731
49.000000       0.038735       0.012674
50.000000       0.038503       0.012616
51.000000       0.038274       0.012558
52.000000       0.038048       0.012499
53.000000       0.037824       0.012439
54.000000       0.037602       0.012379
55.000000       0.037382       0.012318
56.000000       0.037164       0.012257
57.000000       0.036948       0.012195
58.000000       0.036734       0.012133
59.000000       0.036521       0.012072
60.000000       0.036311       0.012010
61.000000       0.036102       0.011947
62.000000       0.035894       0.011885
63.000000       0.035688       0.011823
64.000000       0.035484       0.011761
65.000000       0.035281       0.011699
66.000000       0.035080       0.011637
```

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 67.000000       0.034880       0.011575
 68.000000       0.034681       0.011513
 69.000000       0.034484       0.011452
 70.000000       0.034288       0.011390
 71.000000       0.034093       0.011329
 72.000000       0.033900       0.011268
 73.000000       0.033708       0.011207
 74.000000       0.033517       0.011146
 75.000000       0.033327       0.011086
 76.000000       0.033138       0.011025
 77.000000       0.032951       0.010965
 78.000000       0.032764       0.010906
 79.000000       0.032579       0.010846
 80.000000       0.032395       0.010787
 81.000000       0.032212       0.010728
 82.000000       0.032031       0.010669
 83.000000       0.031850       0.010611
 84.000000       0.031670       0.010553
 85.000000       0.031492       0.010495
 86.000000       0.031314       0.010437
 87.000000       0.031137       0.010380
 88.000000       0.030962       0.010323
 89.000000       0.030788       0.010266
 90.000000       0.030614       0.010210
 91.000000       0.030442       0.010154
 92.000000       0.030270       0.010098
 93.000000       0.030100       0.010042
 94.000000       0.029930       0.009987
 95.000000       0.029762       0.009932
 96.000000       0.029594       0.009877
 97.000000       0.029428       0.009823
 98.000000       0.029262       0.009769
 99.000000       0.029097       0.009715
100.000000       0.028934       0.009661
101.000000       0.028771       0.009608
102.000000       0.028609       0.009555
103.000000       0.028448       0.009503
104.000000       0.028288       0.009450
105.000000       0.028129       0.009398
106.000000       0.027971       0.009346
107.000000       0.027813       0.009295
108.000000       0.027657       0.009244
109.000000       0.027501       0.009193
110.000000       0.027347       0.009142
111.000000       0.027193       0.009091
112.000000       0.027040       0.009041
113.000000       0.026888       0.008991
114.000000       0.026737       0.008942
115.000000       0.026587       0.008893
116.000000       0.026437       0.008843
117.000000       0.026288       0.008795
118.000000       0.026141       0.008746
119.000000       0.025994       0.008698
120.000000       0.025848       0.008650
```

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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 2018-2019

Version: 1.1
Date of this report: 20.04.2020 10:27

Study: ECPA-06A
Description: Appendix A 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	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	0.5	True
DT50_EQ	162	0.003	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	107.805	d	Sorption	Transformation half-life (20°C)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	67.642053	0.006398	0.000000
KOC_EQ	335.298872	0.000182	0.000000
f_NEQ	0.704869	0.027618	0.000000
k_des	0.039600	0.320435	0.452201
DT50_EQ	107.804671	0.000384	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	67.642053	67.629513	67.654594
KOC_EQ	335.298872	335.298515	335.299228
f_NEQ	0.704869	0.650737	0.759000
k_des	0.039600	-0.588453	0.667653
DT50_EQ	107.804671	107.803919	107.805424

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	2.664327
Weighted ME (Chi²)	1.786625
Coeff. of Det. (R²)	0.999031
Model efficiency	0.999025
Abs. deviation	16.582303
Quadr. deviation	29.475746
SRMSE	0.031833
STE	0.017188

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R²)	0.976570	0.992593
Model efficiency	0.976028	0.992577
Abs. deviation	16.564732	0.017571
Quadr. deviation	29.475715	0.000030
SRMSE	0.022527	0.029079
STE	0.017183	0.023147

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R²)	0.987693
Model efficiency	0.986890
Abs. deviation	5.090999
Quadr. deviation	2.167133
SRMSE	0.038620
STE	0.033390

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	66.080000	67.643336	-1.563336	0.00023
0.000	66.740000	67.643336	-0.903336	0.00022
1.000	67.310000	67.215457	0.094543	0.00022
1.000	67.010000	67.215457	-0.205457	0.00022
3.000	67.560000	66.399378	1.160622	0.00022
3.000	67.270000	66.399378	0.870622	0.00022
8.000	64.490000	64.557008	-0.067008	0.00024
8.000	65.290000	64.557008	0.732992	0.00023
14.000	65.040000	62.625973	2.414027	0.00024
14.000	65.690000	62.625973	3.064027	0.00023
28.000	56.520000	58.859796	-2.339796	0.00031
28.000	58.850000	58.859796	-0.009796	0.00029
58.000	51.210000	52.384585	-1.174585	0.00038
58.000	51.430000	52.384585	-0.954585	0.00038
120.000	41.260000	41.650387	-0.390387	0.00059
120.000	42.270000	41.650387	0.619613	0.00056

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.069500	0.067397	0.002103	207.02862
0.000	0.070300	0.067397	0.002903	202.34354
1.000	0.062300	0.065098	-0.002798	257.64630
1.000	0.064100	0.065098	-0.000998	243.37947
3.000	0.060400	0.060935	-0.000535	274.11078
3.000	0.059700	0.060935	-0.001235	280.57653
8.000	0.052400	0.052640	-0.000240	364.19789
8.000	0.053400	0.052640	0.000760	350.68524
14.000	0.046200	0.045614	0.000586	468.50696
14.000	0.046200	0.045614	0.000586	468.50696
28.000	0.034900	0.036368	-0.001468	821.01132
28.000	0.037700	0.036368	0.001332	703.58618
58.000	0.027800	0.028875	-0.001075	1293.92889
58.000	0.029100	0.028875	0.000225	1180.90245
120.000	0.022200	0.022186	0.000014	2029.05608
120.000	0.022900	0.022186	0.000714	1906.90490

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	5.256914	5.785997	-0.529083	207.02862
0.000000	5.242599	5.785997	-0.543398	202.34354
1.000000	6.553173	6.074693	0.478481	257.64630
1.000000	6.202978	6.074693	0.128285	243.37947
3.000000	6.934430	6.646214	0.288216	274.11078
3.000000	7.017007	6.646214	0.370792	280.57653
8.000000	8.056252	8.013233	0.043019	364.19789
8.000000	7.975592	8.013233	-0.037641	350.68524
14.000000	9.826922	9.478834	0.348088	468.50696
14.000000	9.967615	9.478834	0.488780	468.50696
28.000000	11.943842	11.933980	0.009863	821.01132
28.000000	11.359080	11.933980	-0.574900	703.58618
58.000000	14.169863	13.891414	0.278449	1293.92889
58.000000	13.422540	13.891414	-0.468875	1180.90245
120.000000	14.334586	14.522615	-0.188029	2029.05608
120.000000	14.207515	14.522615	-0.315100	1906.90490

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	67.643336	0.067397	5.785997
1.000000	67.215457	0.065098	6.074693
2.000000	66.801086	0.062947	6.361630
3.000000	66.399378	0.060935	6.646214
4.000000	66.009545	0.059051	6.927874
5.000000	65.630851	0.057286	7.206062
6.000000	65.262609	0.055633	7.480262
7.000000	64.904177	0.054084	7.749988
8.000000	64.554956	0.052632	8.014794
9.000000	64.214386	0.051270	8.274268
10.000000	63.881944	0.049991	8.528041
11.000000	63.557144	0.048791	8.775785
12.000000	63.239528	0.047664	9.017211

13.000000	62.928672	0.046605	9.252075
14.000000	62.624178	0.045609	9.480172
15.000000	62.325676	0.044672	9.701338
16.000000	62.032818	0.043790	9.915451
17.000000	61.745282	0.042959	10.122421
18.000000	61.462763	0.042176	10.322199
19.000000	61.184982	0.041438	10.514767
20.000000	60.911672	0.040742	10.700138
21.000000	60.642589	0.040084	10.878355
22.000000	60.377502	0.039462	11.049487
23.000000	60.116197	0.038874	11.213624
24.000000	59.858471	0.038318	11.370882
25.000000	59.604138	0.037791	11.521392
26.000000	59.353021	0.037292	11.665301
27.000000	59.104959	0.036818	11.802773
28.000000	58.859796	0.036368	11.933980
29.000000	58.617391	0.035940	12.059105
30.000000	58.377608	0.035533	12.178340
31.000000	58.140325	0.035146	12.291880
32.000000	57.905422	0.034777	12.399925
33.000000	57.672792	0.034425	12.502679
34.000000	57.442331	0.034089	12.600345
35.000000	57.213946	0.033767	12.693126
36.000000	56.987545	0.033460	12.781227
37.000000	56.763046	0.033165	12.864846
38.000000	56.540370	0.032882	12.944182
39.000000	56.319444	0.032611	13.019428
40.000000	56.100200	0.032351	13.090775
41.000000	55.882574	0.032100	13.158407
42.000000	55.666506	0.031858	13.222503
43.000000	55.451939	0.031626	13.283239
44.000000	55.238821	0.031401	13.340782
45.000000	55.027102	0.031184	13.395296
46.000000	54.816738	0.030974	13.446937
47.000000	54.607683	0.030771	13.495855
48.000000	54.399899	0.030574	13.542197
49.000000	54.193346	0.030383	13.586098
50.000000	53.987989	0.030198	13.627694
51.000000	53.783795	0.030017	13.667109
52.000000	53.580733	0.029842	13.704464
53.000000	53.378772	0.029671	13.739876
54.000000	53.177886	0.029504	13.773452
55.000000	52.978047	0.029341	13.805298
56.000000	52.779233	0.029182	13.835512
57.000000	52.581419	0.029027	13.864188
58.000000	52.384585	0.028875	13.891414
59.000000	52.188709	0.028726	13.917277
60.000000	51.993774	0.028580	13.941854
61.000000	51.799760	0.028437	13.965222
62.000000	51.606651	0.028296	13.987453
63.000000	51.414431	0.028158	14.008613
64.000000	51.223084	0.028022	14.028767
65.000000	51.032597	0.027889	14.047974
66.000000	50.842956	0.027757	14.066292
67.000000	50.654147	0.027628	14.083774
68.000000	50.466160	0.027500	14.100471

69.000000	50.278983	0.027375	14.116430
70.000000	50.092605	0.027251	14.131696
71.000000	49.907015	0.027128	14.146311
72.000000	49.722204	0.027007	14.160316
73.000000	49.538163	0.026887	14.173746
74.000000	49.354883	0.026769	14.186639
75.000000	49.172355	0.026652	14.199026
76.000000	48.990572	0.026537	14.210939
77.000000	48.809526	0.026422	14.222407
78.000000	48.629210	0.026309	14.233458
79.000000	48.449616	0.026197	14.244118
80.000000	48.270740	0.026085	14.254410
81.000000	48.092573	0.025975	14.264358
82.000000	47.915110	0.025866	14.273984
83.000000	47.738345	0.025757	14.283306
84.000000	47.562274	0.025650	14.292345
85.000000	47.386889	0.025543	14.301117
86.000000	47.212187	0.025437	14.309640
87.000000	47.038162	0.025332	14.317930
88.000000	46.864809	0.025228	14.326000
89.000000	46.692124	0.025124	14.333865
90.000000	46.520103	0.025021	14.341537
91.000000	46.348741	0.024919	14.349030
92.000000	46.178034	0.024818	14.356353
93.000000	46.007978	0.024717	14.363518
94.000000	45.838570	0.024616	14.370535
95.000000	45.669805	0.024517	14.377413
96.000000	45.501679	0.024418	14.384161
97.000000	45.334189	0.024319	14.390787
98.000000	45.167333	0.024221	14.397300
99.000000	45.001105	0.024124	14.403705
100.000000	44.835504	0.024027	14.410011
101.000000	44.670525	0.023930	14.416223
102.000000	44.506165	0.023835	14.422348
103.000000	44.342422	0.023739	14.428390
104.000000	44.179293	0.023644	14.434356
105.000000	44.016774	0.023550	14.440251
106.000000	43.854863	0.023456	14.446078
107.000000	43.693556	0.023363	14.451842
108.000000	43.532852	0.023270	14.457548
109.000000	43.372746	0.023177	14.463199
110.000000	43.213237	0.023085	14.468799
111.000000	43.054322	0.022993	14.474350
112.000000	42.895998	0.022902	14.479857
113.000000	42.738263	0.022811	14.485322
114.000000	42.581113	0.022720	14.490748
115.000000	42.424548	0.022630	14.496137
116.000000	42.268563	0.022541	14.501492
117.000000	42.113157	0.022452	14.506816
118.000000	41.958327	0.022363	14.512109
119.000000	41.804071	0.022274	14.517375
120.000000	41.650387	0.022186	14.522615

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g

XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.676459	0.000107
1.000000	0.654761	0.017518
2.000000	0.634422	0.033706
3.000000	0.615351	0.048752
4.000000	0.597466	0.062733
5.000000	0.580686	0.075719
6.000000	0.564939	0.087778
7.000000	0.550157	0.098970
8.000000	0.536275	0.109355
9.000000	0.523234	0.118985
10.000000	0.510978	0.127912
11.000000	0.499455	0.136182
12.000000	0.488618	0.143840
13.000000	0.478419	0.150926
14.000000	0.468818	0.157479
15.000000	0.459775	0.163534
16.000000	0.451252	0.169125
17.000000	0.443216	0.174283
18.000000	0.435635	0.179037
19.000000	0.428477	0.183414
20.000000	0.421716	0.187439
21.000000	0.415326	0.191137
22.000000	0.409281	0.194529
23.000000	0.403560	0.197635
24.000000	0.398140	0.200476
25.000000	0.393003	0.203068
26.000000	0.388129	0.205429
27.000000	0.383502	0.207574
28.000000	0.379105	0.209519
29.000000	0.374923	0.211275
30.000000	0.370942	0.212857
31.000000	0.367149	0.214276
32.000000	0.363532	0.215543
33.000000	0.360079	0.216669
34.000000	0.356780	0.217663
35.000000	0.353624	0.218534
36.000000	0.350603	0.219290
37.000000	0.347708	0.219940
38.000000	0.344930	0.220490
39.000000	0.342262	0.220948
40.000000	0.339697	0.221320
41.000000	0.337229	0.221611
42.000000	0.334851	0.221828
43.000000	0.332557	0.221976
44.000000	0.330342	0.222059
45.000000	0.328202	0.222081
46.000000	0.326131	0.222048
47.000000	0.324125	0.221963
48.000000	0.322181	0.221830
49.000000	0.320293	0.221651
50.000000	0.318459	0.221431
51.000000	0.316676	0.221173
52.000000	0.314940	0.220878

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 53.000000       0.313248       0.220550
 54.000000       0.311598       0.220191
 55.000000       0.309987       0.219803
 56.000000       0.308413       0.219389
 57.000000       0.306873       0.218950
 58.000000       0.305366       0.218488
 59.000000       0.303890       0.218006
 60.000000       0.302443       0.217503
 61.000000       0.301023       0.216983
 62.000000       0.299628       0.216447
 63.000000       0.298258       0.215894
 64.000000       0.296910       0.215328
 65.000000       0.295585       0.214749
 66.000000       0.294279       0.214158
 67.000000       0.292993       0.213556
 68.000000       0.291725       0.212944
 69.000000       0.290474       0.212323
 70.000000       0.289240       0.211694
 71.000000       0.288021       0.211057
 72.000000       0.286817       0.210412
 73.000000       0.285627       0.209762
 74.000000       0.284450       0.209106
 75.000000       0.283286       0.208445
 76.000000       0.282134       0.207779
 77.000000       0.280993       0.207109
 78.000000       0.279863       0.206435
 79.000000       0.278744       0.205759
 80.000000       0.277635       0.205079
 81.000000       0.276536       0.204397
 82.000000       0.275445       0.203712
 83.000000       0.274364       0.203026
 84.000000       0.273291       0.202338
 85.000000       0.272226       0.201649
 86.000000       0.271169       0.200959
 87.000000       0.270119       0.200269
 88.000000       0.269077       0.199577
 89.000000       0.268042       0.198886
 90.000000       0.267013       0.198194
 91.000000       0.265991       0.197502
 92.000000       0.264976       0.196811
 93.000000       0.263966       0.196120
 94.000000       0.262963       0.195429
 95.000000       0.261965       0.194739
 96.000000       0.260973       0.194050
 97.000000       0.259986       0.193362
 98.000000       0.259005       0.192674
 99.000000       0.258029       0.191988
100.000000       0.257058       0.191303
101.000000       0.256092       0.190619
102.000000       0.255131       0.189936
103.000000       0.254175       0.189255
104.000000       0.253223       0.188576
105.000000       0.252276       0.187898
106.000000       0.251333       0.187221
107.000000       0.250395       0.186546
108.000000       0.249461       0.185873
```

109.000000	0.248531	0.185202
110.000000	0.247605	0.184532
111.000000	0.246684	0.183865
112.000000	0.245767	0.183199
113.000000	0.244853	0.182535
114.000000	0.243944	0.181873
115.000000	0.243038	0.181213
116.000000	0.242136	0.180555
117.000000	0.241238	0.179899
118.000000	0.240344	0.179245
119.000000	0.239453	0.178593
120.000000	0.238567	0.177943

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  20.04.2020 10:29

Study: ECPA-06B
Description:   Appendix A 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      62.1    0.0584
14      61.99   0.0586
28      51.8    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       10000   False
cont_OC 0.011   0       10000   False
c_LR    1       0.1     10000   False
M_0     64.7    0       10000   True
ExpFre  0.92    0.01    1.3     False
KOC_EQ  600     0       10000   True
f_NEQ   0.2     0       10000   True
k_des   0.004   0       0.5     True
DT50_EQ 128     0.003   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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	63.072445	0.006316	0.000000
KOC_EQ	312.574633	0.000253	0.000000
f_NEQ	0.605086	0.032878	0.000000
k_des	0.024218	0.579271	0.484029
DT50_EQ	90.195573	0.000922	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	63.072445	63.060066	63.084825
KOC_EQ	312.574633	312.574138	312.575129
f_NEQ	0.605086	0.540645	0.669527
k_des	0.024218	-1.111154	1.159589
DT50_EQ	90.195573	90.193766	90.197379

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	4.413005
Weighted ME (Chi²)	2.919598
Coeff. of Det. (R²)	0.997548
Model efficiency	0.997543
Abs. deviation	20.504308
Quadr. deviation	61.994210
SRMSE	0.051069
STE	0.023510

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R^2)	0.960329	0.979938
Model efficiency	0.960118	0.979702
Abs. deviation	20.470110	0.034198
Quadr. deviation	61.994100	0.000110
SRMSE	0.036147	0.047982
STE	0.023494	0.039195

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R^2)	0.974998
Model efficiency	0.974996
Abs. deviation	4.894578
Quadr. deviation	2.198986
SRMSE	0.057186
STE	0.047188

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	62.540000	63.067396	-0.527396	0.00026
0.000	62.980000	63.067396	-0.087396	0.00025
1.000	61.150000	62.587857	-1.437857	0.00027
1.000	62.690000	62.587857	0.102143	0.00025
3.000	59.190000	61.658367	-2.468367	0.00029
3.000	60.430000	61.658367	-1.228367	0.00027
8.000	59.540000	59.495768	0.044232	0.00028
8.000	58.390000	59.495768	-1.105768	0.00029
14.000	62.100000	57.144825	4.955175	0.00026
14.000	61.990000	57.144825	4.845175	0.00026
28.000	51.800000	52.484117	-0.684117	0.00037
28.000	52.380000	52.484117	-0.104117	0.00036
58.000	45.460000	44.810759	0.649241	0.00048
58.000	43.690000	44.810759	-1.120759	0.00052
120.000	34.030000	33.506983	0.523017	0.00086
120.000	32.920000	33.506983	-0.586983	0.00092

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.078400	0.074025	0.004375	162.69263
0.000	0.080200	0.074025	0.006175	155.47167
1.000	0.069300	0.072408	-0.003108	208.22532
1.000	0.072900	0.072408	0.000492	188.16764
3.000	0.067200	0.069351	-0.002151	221.44274
3.000	0.066100	0.069351	-0.003251	228.87433
8.000	0.060800	0.062642	-0.001842	270.51593
8.000	0.060600	0.062642	-0.002042	272.30446
14.000	0.058400	0.056020	0.002380	293.20698
14.000	0.058600	0.056020	0.002580	291.20898

28.000	0.044600	0.045036	-0.000436	502.72477
28.000	0.045100	0.045036	0.000064	491.63967
58.000	0.034200	0.032700	0.001500	854.96392
58.000	0.031400	0.032700	-0.001300	1014.23993
120.000	0.023600	0.022258	0.001342	1795.46107
120.000	0.021100	0.022258	-0.001158	2246.13104

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	3.691041	4.234442	-0.543401	162.69263
0.000000	3.566868	4.234442	-0.667574	155.47167
1.000000	4.537954	4.358428	0.179525	208.22532
1.000000	4.313451	4.358428	-0.044977	188.16764
3.000000	4.522036	4.605433	-0.083397	221.44274
3.000000	4.856209	4.605433	0.250776	228.87433
8.000000	5.506763	5.212386	0.294377	270.51593
8.000000	5.349314	5.212386	0.136927	272.30446
14.000000	6.347562	5.915553	0.432008	293.20698
14.000000	6.292498	5.915553	0.376945	291.20898
28.000000	7.328350	7.368595	-0.040246	502.72477
28.000000	7.328191	7.368595	-0.040405	491.63967
58.000000	9.006398	9.418412	-0.412014	854.96392
58.000000	9.628013	9.418412	0.209601	1014.23993
120.000000	10.133492	10.768533	-0.635042	1795.46107
120.000000	11.315896	10.768533	0.547362	2246.13104

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	63.067396	0.074025	4.234442
1.000000	62.587857	0.072408	4.358428
2.000000	62.118300	0.070851	4.482119
3.000000	61.658367	0.069351	4.605433
4.000000	61.207714	0.067906	4.728291
5.000000	60.766009	0.066513	4.850616
6.000000	60.332934	0.065171	4.972332
7.000000	59.908185	0.063877	5.093362
8.000000	59.491468	0.062630	5.213635
9.000000	59.082502	0.061427	5.333080
10.000000	58.681015	0.060266	5.451627
11.000000	58.286749	0.059147	5.569211
12.000000	57.899454	0.058067	5.685767
13.000000	57.518889	0.057025	5.801234
14.000000	57.144825	0.056020	5.915553
15.000000	56.777040	0.055049	6.028669
16.000000	56.415322	0.054111	6.140528
17.000000	56.059466	0.053206	6.251080
18.000000	55.709276	0.052331	6.360278
19.000000	55.364565	0.051486	6.468077
20.000000	55.025149	0.050669	6.574437
21.000000	54.690857	0.049879	6.679320
22.000000	54.361519	0.049116	6.782689
23.000000	54.036976	0.048378	6.884514
24.000000	53.717074	0.047663	6.984766
25.000000	53.401663	0.046972	7.083418
26.000000	53.090602	0.046304	7.180448

27.000000	52.783752	0.045656	7.275835
28.000000	52.480984	0.045029	7.369563
29.000000	52.182169	0.044422	7.461617
30.000000	51.887186	0.043834	7.551986
31.000000	51.595919	0.043264	7.640660
32.000000	51.308254	0.042711	7.727633
33.000000	51.024084	0.042175	7.812902
34.000000	50.743305	0.041655	7.896465
35.000000	50.465817	0.041151	7.978322
36.000000	50.191523	0.040661	8.058478
37.000000	49.920332	0.040186	8.136936
38.000000	49.652155	0.039725	8.213704
39.000000	49.386906	0.039277	8.288791
40.000000	49.124502	0.038841	8.362207
41.000000	48.864866	0.038418	8.433966
42.000000	48.607921	0.038006	8.504081
43.000000	48.353594	0.037606	8.572568
44.000000	48.101815	0.037217	8.639444
45.000000	47.852515	0.036838	8.704726
46.000000	47.605631	0.036469	8.768435
47.000000	47.361098	0.036110	8.830590
48.000000	47.118858	0.035760	8.891213
49.000000	46.878851	0.035419	8.950326
50.000000	46.641023	0.035086	9.007953
51.000000	46.405319	0.034762	9.064117
52.000000	46.171687	0.034446	9.118842
53.000000	45.940078	0.034137	9.172153
54.000000	45.710445	0.033836	9.224077
55.000000	45.482739	0.033542	9.274638
56.000000	45.256918	0.033255	9.323863
57.000000	45.032938	0.032974	9.371779
58.000000	44.810759	0.032700	9.418412
59.000000	44.590339	0.032432	9.463788
60.000000	44.371642	0.032169	9.507935
61.000000	44.154629	0.031912	9.550880
62.000000	43.939266	0.031661	9.592650
63.000000	43.725518	0.031415	9.633270
64.000000	43.513352	0.031174	9.672770
65.000000	43.302737	0.030938	9.711174
66.000000	43.093640	0.030707	9.748509
67.000000	42.886034	0.030480	9.784802
68.000000	42.679889	0.030258	9.820078
69.000000	42.475177	0.030040	9.854364
70.000000	42.271873	0.029826	9.887685
71.000000	42.069949	0.029616	9.920065
72.000000	41.869383	0.029409	9.951531
73.000000	41.670148	0.029207	9.982105
74.000000	41.472224	0.029007	10.011813
75.000000	41.275586	0.028812	10.040678
76.000000	41.080213	0.028619	10.068724
77.000000	40.886086	0.028430	10.095972
78.000000	40.693183	0.028244	10.122446
79.000000	40.501485	0.028061	10.148168
80.000000	40.310973	0.027881	10.173159
81.000000	40.121629	0.027703	10.197441
82.000000	39.933436	0.027528	10.221034

83.000000	39.746376	0.027356	10.243958
84.000000	39.560433	0.027186	10.266234
85.000000	39.375591	0.027019	10.287880
86.000000	39.191835	0.026854	10.308916
87.000000	39.009150	0.026692	10.329360
88.000000	38.827520	0.026531	10.349231
89.000000	38.646933	0.026373	10.368545
90.000000	38.467374	0.026217	10.387320
91.000000	38.288831	0.026063	10.405572
92.000000	38.111290	0.025911	10.423319
93.000000	37.934740	0.025761	10.440575
94.000000	37.759168	0.025612	10.457357
95.000000	37.584562	0.025466	10.473679
96.000000	37.410912	0.025321	10.489556
97.000000	37.238206	0.025177	10.505001
98.000000	37.066433	0.025036	10.520030
99.000000	36.895584	0.024896	10.534656
100.000000	36.725649	0.024757	10.548890
101.000000	36.556616	0.024621	10.562747
102.000000	36.388478	0.024485	10.576239
103.000000	36.221224	0.024351	10.589376
104.000000	36.054846	0.024218	10.602172
105.000000	35.889335	0.024087	10.614637
106.000000	35.724683	0.023957	10.626783
107.000000	35.560880	0.023828	10.638619
108.000000	35.397920	0.023701	10.650156
109.000000	35.235793	0.023574	10.661404
110.000000	35.074493	0.023449	10.672373
111.000000	34.914013	0.023325	10.683072
112.000000	34.754343	0.023202	10.693510
113.000000	34.595479	0.023081	10.703696
114.000000	34.437412	0.022960	10.713639
115.000000	34.280135	0.022840	10.723346
116.000000	34.123643	0.022722	10.732826
117.000000	33.967929	0.022604	10.742086
118.000000	33.812986	0.022487	10.751134
119.000000	33.658808	0.022372	10.759977
120.000000	33.505389	0.022257	10.768622

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.630724	0.000090
1.000000	0.617492	0.008521
2.000000	0.604737	0.016577
3.000000	0.592439	0.024271
4.000000	0.580580	0.031619
5.000000	0.569143	0.038634
6.000000	0.558112	0.045330
7.000000	0.547470	0.051721
8.000000	0.537202	0.057818
9.000000	0.527293	0.063634
10.000000	0.517729	0.069179

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11.000000       0.508497       0.074465
12.000000       0.499583       0.079503
13.000000       0.490974       0.084303
14.000000       0.482660       0.088873
15.000000       0.474628       0.093225
16.000000       0.466867       0.097366
17.000000       0.459366       0.101305
18.000000       0.452116       0.105051
19.000000       0.445107       0.108611
20.000000       0.438328       0.111993
21.000000       0.431771       0.115204
22.000000       0.425428       0.118252
23.000000       0.419290       0.121143
24.000000       0.413349       0.123883
25.000000       0.407597       0.126479
26.000000       0.402027       0.128936
27.000000       0.396631       0.131261
28.000000       0.391404       0.133459
29.000000       0.386339       0.135535
30.000000       0.381428       0.137494
31.000000       0.376667       0.139341
32.000000       0.372050       0.141080
33.000000       0.367570       0.142717
34.000000       0.363223       0.144255
35.000000       0.359003       0.145698
36.000000       0.354906       0.147051
37.000000       0.350927       0.148317
38.000000       0.347062       0.149500
39.000000       0.343305       0.150603
40.000000       0.339653       0.151630
41.000000       0.336102       0.152583
42.000000       0.332648       0.153467
43.000000       0.329287       0.154283
44.000000       0.326016       0.155036
45.000000       0.322832       0.155726
46.000000       0.319730       0.156358
47.000000       0.316709       0.156933
48.000000       0.313764       0.157455
49.000000       0.310894       0.157924
50.000000       0.308094       0.158345
51.000000       0.305364       0.158717
52.000000       0.302699       0.159045
53.000000       0.300098       0.159329
54.000000       0.297559       0.159572
55.000000       0.295078       0.159775
56.000000       0.292654       0.159940
57.000000       0.290285       0.160068
58.000000       0.287969       0.160162
59.000000       0.285703       0.160223
60.000000       0.283487       0.160252
61.000000       0.281317       0.160251
62.000000       0.279193       0.160221
63.000000       0.277113       0.160163
64.000000       0.275075       0.160079
65.000000       0.273078       0.159970
66.000000       0.271120       0.159836
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 67.000000       0.269200       0.159680
 68.000000       0.267317       0.159501
 69.000000       0.265469       0.159302
 70.000000       0.263655       0.159083
 71.000000       0.261873       0.158844
 72.000000       0.260124       0.158588
 73.000000       0.258405       0.158314
 74.000000       0.256716       0.158024
 75.000000       0.255055       0.157718
 76.000000       0.253422       0.157397
 77.000000       0.251815       0.157062
 78.000000       0.250235       0.156714
 79.000000       0.248679       0.156352
 80.000000       0.247147       0.155979
 81.000000       0.245638       0.155593
 82.000000       0.244153       0.155197
 83.000000       0.242688       0.154791
 84.000000       0.241245       0.154374
 85.000000       0.239823       0.153948
 86.000000       0.238420       0.153513
 87.000000       0.237036       0.153070
 88.000000       0.235671       0.152619
 89.000000       0.234324       0.152160
 90.000000       0.232994       0.151694
 91.000000       0.231681       0.151221
 92.000000       0.230384       0.150742
 93.000000       0.229103       0.150257
 94.000000       0.227838       0.149767
 95.000000       0.226587       0.149271
 96.000000       0.225352       0.148770
 97.000000       0.224130       0.148265
 98.000000       0.222922       0.147755
 99.000000       0.221727       0.147242
100.000000       0.220545       0.146724
101.000000       0.219375       0.146203
102.000000       0.218218       0.145679
103.000000       0.217073       0.145151
104.000000       0.215939       0.144621
105.000000       0.214816       0.144089
106.000000       0.213705       0.143554
107.000000       0.212604       0.143017
108.000000       0.211513       0.142477
109.000000       0.210433       0.141936
110.000000       0.209362       0.141394
111.000000       0.208301       0.140850
112.000000       0.207250       0.140305
113.000000       0.206207       0.139758
114.000000       0.205174       0.139211
115.000000       0.204149       0.138663
116.000000       0.203133       0.138114
117.000000       0.202125       0.137565
118.000000       0.201125       0.137015
119.000000       0.200133       0.136465
120.000000       0.199150       0.135915
```

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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 2018-2019

Version: 1.1
Date of this report: 20.04.2020 10:32

Study: ECPA-06C
Description: Appendix A 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	0.0547
3	64.42	0.0551
8	64.69	0.0502
8	63.78	0.0498
14	68.64	0.047
14	67.96	0.0468
28	60.5	0.0389
28	59.67	0.039
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	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	0.5	True
DT50_EQ	128	0.003	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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	67.000404	0.002146	0.000000
KOC_EQ	396.421086	0.000208	0.000000
f_NEQ	0.597829	0.043906	0.000000
k_des	0.045645	0.272424	0.432487
DT50_EQ	175.791707	0.000206	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	67.000404	66.996198	67.004611
KOC_EQ	396.421086	396.420677	396.421494
f_NEQ	0.597829	0.511774	0.683885
k_des	0.045645	-0.488306	0.579597
DT50_EQ	175.791707	175.791303	175.792110

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	4.141516
Weighted ME (Chi²)	2.882180
Coeff. of Det. (R²)	0.997595
Model efficiency	0.997568
Abs. deviation	29.532724
Quadr. deviation	76.899626
SRMSE	0.049808
STE	0.029653

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R²)	0.896735	0.982438
Model efficiency	0.892046	0.982378
Abs. deviation	29.511193	0.021531
Quadr. deviation	76.899584	0.000042
SRMSE	0.035246	0.034366
STE	0.029654	0.028502

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R²)	0.975693
Model efficiency	0.970442
Abs. deviation	5.653173
Quadr. deviation	2.748411
SRMSE	0.043753
STE	0.037299

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	66.260000	66.999709	-0.739709	0.00023
0.000	68.420000	66.999709	1.420291	0.00021
1.000	68.240000	66.739357	1.500643	0.00021
1.000	69.110000	66.739357	2.370643	0.00021
3.000	66.000000	66.240296	-0.240296	0.00023
3.000	64.420000	66.240296	-1.820296	0.00024
8.000	64.690000	65.099463	-0.409463	0.00024
8.000	63.780000	65.099463	-1.319463	0.00025
14.000	68.640000	63.878228	4.761772	0.00021
14.000	67.960000	63.878228	4.081772	0.00022
28.000	60.500000	61.406580	-0.906580	0.00027
28.000	59.670000	61.406580	-1.736580	0.00028
58.000	54.040000	56.886844	-2.846844	0.00034
58.000	55.020000	56.886844	-1.866844	0.00033
120.000	47.480000	48.818274	-1.338274	0.00044
120.000	50.970000	48.818274	2.151726	0.00038

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.063300	0.062579	0.000721	249.57012
0.000	0.065400	0.062579	0.002821	233.80000
1.000	0.060800	0.060742	0.000058	270.51593
1.000	0.062200	0.060742	0.001458	258.47541
3.000	0.054700	0.057430	-0.002730	334.21455
3.000	0.055100	0.057430	-0.002330	329.37968
8.000	0.050200	0.050902	-0.000702	396.81910
8.000	0.049800	0.050902	-0.001102	403.21930
14.000	0.047000	0.045473	0.001527	452.69353
14.000	0.046800	0.045473	0.001327	456.57097
28.000	0.038900	0.038546	0.000354	660.84681
28.000	0.039000	0.038546	0.000454	657.46220
58.000	0.032100	0.033172	-0.001072	970.48748
58.000	0.031300	0.033172	-0.001872	1020.73105
120.000	0.027900	0.028108	-0.000208	1284.67003
120.000	0.030900	0.028108	0.002792	1047.32879

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	6.151615	6.390744	-0.239129	249.57012
0.000000	6.145774	6.390744	-0.244970	233.80000
1.000000	6.907684	6.671688	0.235997	270.51593
1.000000	6.794932	6.671688	0.123245	258.47541
3.000000	7.749814	7.218399	0.531415	334.21455
3.000000	7.375470	7.218399	0.157071	329.37968
8.000000	8.570454	8.473359	0.097095	396.81910
8.000000	8.491229	8.473359	0.017870	403.21930
14.000000	10.288255	9.731892	0.556364	452.69353
14.000000	10.205368	9.731892	0.473476	456.57097
28.000000	11.236699	11.614857	-0.378158	660.84681
28.000000	10.984000	11.614857	-0.630857	657.46220
58.000000	12.518891	12.833177	-0.314286	970.48748
58.000000	13.262275	12.833177	0.429098	1020.73105
120.000000	12.701921	13.052605	-0.350684	1284.67003
120.000000	12.179146	13.052605	-0.873459	1047.32879

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	66.999709	0.062579	6.390744
1.000000	66.739357	0.060742	6.671688
2.000000	66.486384	0.059028	6.947754
3.000000	66.240296	0.057430	7.218399
4.000000	66.000635	0.055938	7.483126
5.000000	65.766976	0.054546	7.741491
6.000000	65.538921	0.053245	7.993100
7.000000	65.316103	0.052031	8.237615
8.000000	65.098180	0.050896	8.474748
9.000000	64.884833	0.049835	8.704268
10.000000	64.675766	0.048842	8.925992
11.000000	64.470704	0.047914	9.139789
12.000000	64.269392	0.047045	9.345575

13.000000	64.071591	0.046231	9.543310
14.000000	63.877080	0.045468	9.732997
15.000000	63.685654	0.044753	9.914676
16.000000	63.497121	0.044082	10.088423
17.000000	63.311304	0.043453	10.254345
18.000000	63.128037	0.042862	10.412577
19.000000	62.947167	0.042306	10.563277
20.000000	62.768550	0.041783	10.706625
21.000000	62.592054	0.041292	10.842820
22.000000	62.417554	0.040828	10.972074
23.000000	62.244936	0.040392	11.094610
24.000000	62.074093	0.039980	11.210661
25.000000	61.904925	0.039591	11.320467
26.000000	61.737340	0.039223	11.424271
27.000000	61.571252	0.038875	11.522319
28.000000	61.406580	0.038546	11.614857
29.000000	61.243250	0.038234	11.702130
30.000000	61.081192	0.037938	11.784381
31.000000	60.920343	0.037657	11.861849
32.000000	60.760642	0.037390	11.934767
33.000000	60.602033	0.037136	12.003364
34.000000	60.444465	0.036893	12.067862
35.000000	60.287889	0.036662	12.128476
36.000000	60.132259	0.036441	12.185415
37.000000	59.977534	0.036230	12.238879
38.000000	59.823676	0.036028	12.289061
39.000000	59.670647	0.035834	12.336145
40.000000	59.518414	0.035648	12.380310
41.000000	59.366945	0.035469	12.421722
42.000000	59.216211	0.035298	12.460545
43.000000	59.066184	0.035132	12.496931
44.000000	58.916840	0.034972	12.531026
45.000000	58.768154	0.034818	12.562967
46.000000	58.620105	0.034669	12.592888
47.000000	58.472670	0.034524	12.620910
48.000000	58.325833	0.034384	12.647153
49.000000	58.179573	0.034249	12.671726
50.000000	58.033876	0.034117	12.694735
51.000000	57.888724	0.033988	12.716277
52.000000	57.744104	0.033863	12.736447
53.000000	57.600002	0.033741	12.755330
54.000000	57.456405	0.033622	12.773011
55.000000	57.313302	0.033506	12.789565
56.000000	57.170680	0.033393	12.805066
57.000000	57.028531	0.033281	12.819582
58.000000	56.886844	0.033172	12.833177
59.000000	56.745609	0.033065	12.845911
60.000000	56.604820	0.032960	12.857841
61.000000	56.464467	0.032857	12.869018
62.000000	56.324543	0.032756	12.879494
63.000000	56.185042	0.032656	12.889313
64.000000	56.045956	0.032558	12.898520
65.000000	55.907280	0.032461	12.907155
66.000000	55.769008	0.032366	12.915256
67.000000	55.631134	0.032271	12.922858
68.000000	55.493654	0.032178	12.929995

69.000000	55.356562	0.032086	12.936697
70.000000	55.219853	0.031995	12.942994
71.000000	55.083525	0.031905	12.948913
72.000000	54.947573	0.031816	12.954479
73.000000	54.811992	0.031728	12.959716
74.000000	54.676780	0.031641	12.964646
75.000000	54.541933	0.031554	12.969290
76.000000	54.407448	0.031469	12.973666
77.000000	54.273322	0.031384	12.977793
78.000000	54.139551	0.031299	12.981688
79.000000	54.006134	0.031215	12.985366
80.000000	53.873068	0.031132	12.988841
81.000000	53.740350	0.031050	12.992129
82.000000	53.607977	0.030968	12.995241
83.000000	53.475949	0.030886	12.998189
84.000000	53.344262	0.030805	13.000984
85.000000	53.212914	0.030724	13.003637
86.000000	53.081905	0.030644	13.006157
87.000000	52.951230	0.030565	13.008553
88.000000	52.820890	0.030485	13.010834
89.000000	52.690882	0.030407	13.013007
90.000000	52.561205	0.030328	13.015080
91.000000	52.431857	0.030250	13.017060
92.000000	52.302836	0.030172	13.018953
93.000000	52.174141	0.030095	13.020764
94.000000	52.045771	0.030018	13.022500
95.000000	51.917725	0.029941	13.024165
96.000000	51.790000	0.029865	13.025764
97.000000	51.662595	0.029789	13.027303
98.000000	51.535511	0.029713	13.028784
99.000000	51.408744	0.029637	13.030212
100.000000	51.282294	0.029562	13.031590
101.000000	51.156161	0.029487	13.032922
102.000000	51.030341	0.029412	13.034211
103.000000	50.904836	0.029338	13.035460
104.000000	50.779643	0.029264	13.036671
105.000000	50.654762	0.029190	13.037848
106.000000	50.530191	0.029116	13.038992
107.000000	50.405930	0.029043	13.040106
108.000000	50.281977	0.028969	13.041192
109.000000	50.158332	0.028896	13.042251
110.000000	50.034994	0.028824	13.043286
111.000000	49.911961	0.028751	13.044298
112.000000	49.789233	0.028679	13.045289
113.000000	49.666808	0.028607	13.046260
114.000000	49.544687	0.028535	13.047213
115.000000	49.422868	0.028463	13.048148
116.000000	49.301350	0.028392	13.049067
117.000000	49.180133	0.028320	13.049972
118.000000	49.059215	0.028249	13.050862
119.000000	48.938595	0.028178	13.051740
120.000000	48.818274	0.028108	13.052605

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g

XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.670013	0.000104
1.000000	0.650645	0.016860
2.000000	0.632573	0.032395
3.000000	0.615706	0.046794
4.000000	0.599959	0.060138
5.000000	0.585254	0.072501
6.000000	0.571516	0.083952
7.000000	0.558680	0.094555
8.000000	0.546680	0.104371
9.000000	0.535458	0.113455
10.000000	0.524960	0.121858
11.000000	0.515135	0.129629
12.000000	0.505935	0.136812
13.000000	0.497317	0.143449
14.000000	0.489239	0.149578
15.000000	0.481665	0.155236
16.000000	0.474558	0.160455
17.000000	0.467885	0.165266
18.000000	0.461617	0.169699
19.000000	0.455725	0.173780
20.000000	0.450183	0.177534
21.000000	0.444966	0.180985
22.000000	0.440051	0.184153
23.000000	0.435418	0.187058
24.000000	0.431046	0.189720
25.000000	0.426918	0.192156
26.000000	0.423016	0.194380
27.000000	0.419324	0.196410
28.000000	0.415828	0.198258
29.000000	0.412515	0.199937
30.000000	0.409371	0.201459
31.000000	0.406385	0.202835
32.000000	0.403546	0.204077
33.000000	0.400844	0.205193
34.000000	0.398268	0.206192
35.000000	0.395811	0.207082
36.000000	0.393464	0.207872
37.000000	0.391220	0.208569
38.000000	0.389071	0.209178
39.000000	0.387011	0.209708
40.000000	0.385034	0.210162
41.000000	0.383134	0.210547
42.000000	0.381305	0.210867
43.000000	0.379544	0.211128
44.000000	0.377845	0.211333
45.000000	0.376204	0.211487
46.000000	0.374618	0.211593
47.000000	0.373081	0.211654
48.000000	0.371592	0.211675
49.000000	0.370147	0.211657
50.000000	0.368743	0.211604
51.000000	0.367377	0.211518
52.000000	0.366047	0.211402

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 53.000000       0.364750       0.211257
 54.000000       0.363485       0.211087
 55.000000       0.362248       0.210892
 56.000000       0.361039       0.210675
 57.000000       0.359855       0.210438
 58.000000       0.358694       0.210181
 59.000000       0.357556       0.209907
 60.000000       0.356439       0.209616
 61.000000       0.355341       0.209310
 62.000000       0.354262       0.208990
 63.000000       0.353200       0.208657
 64.000000       0.352154       0.208312
 65.000000       0.351122       0.207956
 66.000000       0.350105       0.207591
 67.000000       0.349102       0.207215
 68.000000       0.348111       0.206832
 69.000000       0.347131       0.206440
 70.000000       0.346163       0.206041
 71.000000       0.345205       0.205636
 72.000000       0.344257       0.205224
 73.000000       0.343319       0.204807
 74.000000       0.342389       0.204385
 75.000000       0.341467       0.203958
 76.000000       0.340554       0.203526
 77.000000       0.339647       0.203091
 78.000000       0.338748       0.202653
 79.000000       0.337856       0.202211
 80.000000       0.336970       0.201766
 81.000000       0.336090       0.201319
 82.000000       0.335215       0.200870
 83.000000       0.334347       0.200418
 84.000000       0.333483       0.199965
 85.000000       0.332625       0.199510
 86.000000       0.331771       0.199053
 87.000000       0.330922       0.198595
 88.000000       0.330077       0.198137
 89.000000       0.329237       0.197677
 90.000000       0.328401       0.197216
 91.000000       0.327568       0.196755
 92.000000       0.326740       0.196294
 93.000000       0.325915       0.195832
 94.000000       0.325093       0.195369
 95.000000       0.324275       0.194907
 96.000000       0.323461       0.194444
 97.000000       0.322649       0.193982
 98.000000       0.321841       0.193519
 99.000000       0.321036       0.193057
100.000000       0.320233       0.192595
101.000000       0.319434       0.192133
102.000000       0.318637       0.191671
103.000000       0.317843       0.191210
104.000000       0.317052       0.190749
105.000000       0.316263       0.190289
106.000000       0.315477       0.189830
107.000000       0.314694       0.189370
108.000000       0.313912       0.188912
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109.000000	0.313134	0.188454
110.000000	0.312357	0.187997
111.000000	0.311583	0.187541
112.000000	0.310812	0.187085
113.000000	0.310042	0.186630
114.000000	0.309275	0.186176
115.000000	0.308510	0.185723
116.000000	0.307748	0.185270
117.000000	0.306987	0.184819
118.000000	0.306229	0.184368
119.000000	0.305472	0.183918
120.000000	0.304718	0.183469

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  20.04.2020 10:35

Study: ECPA-06D
Description:   Appendix A 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      0.0221
58      43.88   0.021
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       10000   False
cont_OC 0.018   0       10000   False
c_LR    1       0.1     10000   False
M_0     67      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       0.5     True
DT50_EQ 115     0.003   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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	65.945758	0.009096	0.000000
KOC_EQ	318.403485	0.000311	0.000000
f_NEQ	0.667642	0.033823	0.000000
k_des	0.027781	0.559698	0.480049
DT50_EQ	78.682643	0.001121	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	65.945758	65.927931	65.963586
KOC_EQ	318.403485	318.402877	318.404094
f_NEQ	0.667642	0.601349	0.733934
k_des	0.027781	-1.069227	1.124789
DT50_EQ	78.682643	78.680446	78.684840

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	32
No act. param.	5
Deg. of Freedom	11
Model error (Chi²)	3.486162
Weighted ME (Chi²)	2.890002
Coeff. of Det. (R²)	0.998124
Model efficiency	0.998114
Abs. deviation	20.380489
Quadr. deviation	51.300694
SRMSE	0.045000
STE	0.022636

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	16	16
Coeff. of Det. (R^2)	0.973660	0.986049
Model efficiency	0.973503	0.985979
Abs. deviation	20.359895	0.020593
Quadr. deviation	51.300647	0.000047
SRMSE	0.031842	0.043720
STE	0.022629	0.032807

	App. sorp. coeff. (mL/g)
No obs.	16
Coeff. of Det. (R^2)	0.988367
Model efficiency	0.988090
Abs. deviation	5.273317
Quadr. deviation	2.849938
SRMSE	0.037067
STE	0.028946

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	64.070000	65.940917	-1.870917	0.00024
0.000	65.390000	65.940917	-0.550917	0.00023
1.000	63.970000	65.367608	-1.397608	0.00024
1.000	68.270000	65.367608	2.902392	0.00021
3.000	62.640000	64.264431	-1.624431	0.00025
3.000	63.460000	64.264431	-0.804431	0.00025
8.000	61.610000	61.735997	-0.125997	0.00026
8.000	61.580000	61.735997	-0.155997	0.00026
14.000	62.310000	59.046037	3.263963	0.00026
14.000	63.510000	59.046037	4.463963	0.00025
28.000	53.550000	53.844059	-0.294059	0.00035
28.000	53.350000	53.844059	-0.494059	0.00035
58.000	46.000000	45.484285	0.515715	0.00047
58.000	43.880000	45.484285	-1.604285	0.00052
120.000	33.060000	33.220580	-0.160580	0.00091
120.000	33.090000	33.220580	-0.130580	0.00091

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.056900	0.055676	0.001224	308.86981
0.000	0.056900	0.055676	0.001224	308.86981
1.000	0.053300	0.054148	-0.000848	352.00237
1.000	0.054600	0.054148	0.000452	335.43990
3.000	0.049900	0.051296	-0.001396	401.60481
3.000	0.049300	0.051296	-0.001996	411.43967
8.000	0.044400	0.045216	-0.000816	507.26402
8.000	0.043800	0.045216	-0.001416	521.25685
14.000	0.044300	0.039486	0.004814	509.55674
14.000	0.042300	0.039486	0.002814	558.88090

28.000	0.029100	0.030637	-0.001537	1180.90245
28.000	0.030100	0.030637	-0.000537	1103.74058
58.000	0.022100	0.021780	0.000320	2047.46013
58.000	0.021000	0.021780	-0.000780	2267.57370
120.000	0.014800	0.014641	0.000159	4565.37619
120.000	0.014900	0.014641	0.000259	4504.30161

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	6.891105	7.475653	-0.584547	308.86981
0.000000	7.123091	7.475653	-0.352561	308.86981
1.000000	7.632876	7.703979	-0.071102	352.00237
1.000000	8.134663	7.703979	0.430684	335.43990
3.000000	8.184106	8.160113	0.023993	401.60481
3.000000	8.503211	8.160113	0.343098	411.43967
8.000000	9.507126	9.285340	0.221786	507.26402
8.000000	9.690361	9.285340	0.405020	521.25685
14.000000	9.696463	10.585488	-0.889025	509.55674
14.000000	10.645184	10.585488	0.059697	558.88090
28.000000	14.033062	13.206522	0.826540	1180.90245
28.000000	13.355252	13.206522	0.148731	1103.74058
58.000000	16.445480	16.515155	-0.069676	2047.46013
58.000000	16.526238	16.515155	0.011083	2267.57370
120.000000	17.968838	18.321833	-0.352995	4565.37619
120.000000	17.839054	18.321833	-0.482779	4504.30161

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	65.940917	0.055676	7.475653
1.000000	65.367608	0.054148	7.703979
2.000000	64.808993	0.052689	7.932206
3.000000	64.264431	0.051296	8.160113
4.000000	63.733312	0.049965	8.387477
5.000000	63.215052	0.048694	8.614080
6.000000	62.709098	0.047479	8.839707
7.000000	62.214921	0.046318	9.064146
8.000000	61.732018	0.045207	9.287193
9.000000	61.259910	0.044146	9.508646
10.000000	60.798140	0.043130	9.728312
11.000000	60.346272	0.042159	9.946004
12.000000	59.903892	0.041229	10.161543
13.000000	59.470606	0.040339	10.374759
14.000000	59.046037	0.039486	10.585488
15.000000	58.629825	0.038670	10.793577
16.000000	58.221631	0.037888	10.998883
17.000000	57.821127	0.037138	11.201272
18.000000	57.428005	0.036419	11.400618
19.000000	57.041967	0.035730	11.596808
20.000000	56.662733	0.035068	11.789737
21.000000	56.290033	0.034434	11.979310
22.000000	55.923613	0.033824	12.165444
23.000000	55.563228	0.033239	12.348063
24.000000	55.208645	0.032677	12.527104
25.000000	54.859643	0.032137	12.702511
26.000000	54.516011	0.031618	12.874239

27.000000	54.177547	0.031118	13.042252
28.000000	53.844059	0.030637	13.206522
29.000000	53.515364	0.030175	13.367029
30.000000	53.191287	0.029729	13.523765
31.000000	52.871663	0.029300	13.676724
32.000000	52.556332	0.028887	13.825912
33.000000	52.245142	0.028488	13.971340
34.000000	51.937950	0.028103	14.113027
35.000000	51.634618	0.027732	14.250996
36.000000	51.335014	0.027374	14.385278
37.000000	51.039013	0.027028	14.515909
38.000000	50.746496	0.026693	14.642928
39.000000	50.457347	0.026370	14.766380
40.000000	50.171459	0.026057	14.886315
41.000000	49.888727	0.025755	15.002786
42.000000	49.609052	0.025462	15.115849
43.000000	49.332340	0.025178	15.225562
44.000000	49.058500	0.024903	15.331989
45.000000	48.787445	0.024636	15.435192
46.000000	48.519093	0.024377	15.535239
47.000000	48.253367	0.024126	15.632197
48.000000	47.990189	0.023883	15.726136
49.000000	47.729489	0.023646	15.817125
50.000000	47.471197	0.023416	15.905236
51.000000	47.215249	0.023192	15.990541
52.000000	46.961581	0.022974	16.073112
53.000000	46.710134	0.022762	16.153020
54.000000	46.460850	0.022556	16.230339
55.000000	46.213674	0.022354	16.305141
56.000000	45.968555	0.022158	16.377497
57.000000	45.725441	0.021967	16.447478
58.000000	45.484285	0.021780	16.515155
59.000000	45.245042	0.021598	16.580598
60.000000	45.007666	0.021420	16.643876
61.000000	44.772117	0.021246	16.705055
62.000000	44.538353	0.021076	16.764204
63.000000	44.306336	0.020910	16.821388
64.000000	44.076030	0.020747	16.876671
65.000000	43.847399	0.020587	16.930117
66.000000	43.620408	0.020431	16.981787
67.000000	43.395026	0.020278	17.031741
68.000000	43.171221	0.020128	17.080039
69.000000	42.948963	0.019981	17.126739
70.000000	42.728223	0.019837	17.171897
71.000000	42.508975	0.019695	17.215567
72.000000	42.291190	0.019556	17.257803
73.000000	42.074845	0.019419	17.298656
74.000000	41.859915	0.019285	17.338178
75.000000	41.646375	0.019153	17.376416
76.000000	41.434204	0.019023	17.413419
77.000000	41.223380	0.018895	17.449233
78.000000	41.013881	0.018769	17.483902
79.000000	40.805689	0.018645	17.517469
80.000000	40.598783	0.018523	17.549977
81.000000	40.393144	0.018403	17.581465
82.000000	40.188756	0.018284	17.611974

83.000000	39.985600	0.018167	17.641541
84.000000	39.783660	0.018052	17.670202
85.000000	39.582920	0.017938	17.697993
86.000000	39.383365	0.017826	17.724949
87.000000	39.184978	0.017715	17.751101
88.000000	38.987747	0.017606	17.776483
89.000000	38.791656	0.017498	17.801124
90.000000	38.596693	0.017391	17.825054
91.000000	38.402844	0.017286	17.848301
92.000000	38.210096	0.017182	17.870894
93.000000	38.018438	0.017079	17.892858
94.000000	37.827857	0.016977	17.914219
95.000000	37.638342	0.016876	17.935001
96.000000	37.449882	0.016776	17.955229
97.000000	37.262467	0.016678	17.974924
98.000000	37.076084	0.016580	17.994108
99.000000	36.890725	0.016483	18.012803
100.000000	36.706380	0.016387	18.031028
101.000000	36.523038	0.016293	18.048803
102.000000	36.340692	0.016199	18.066147
103.000000	36.159330	0.016106	18.083078
104.000000	35.978945	0.016014	18.099612
105.000000	35.799529	0.015922	18.115766
106.000000	35.621072	0.015832	18.131557
107.000000	35.443566	0.015742	18.146998
108.000000	35.267004	0.015653	18.162106
109.000000	35.091378	0.015565	18.176894
110.000000	34.916680	0.015478	18.191375
111.000000	34.742902	0.015391	18.205563
112.000000	34.570039	0.015305	18.219469
113.000000	34.398082	0.015220	18.233107
114.000000	34.227024	0.015135	18.246486
115.000000	34.056859	0.015051	18.259619
116.000000	33.887581	0.014968	18.272515
117.000000	33.719182	0.014885	18.285185
118.000000	33.551657	0.014803	18.297638
119.000000	33.384999	0.014721	18.309884
120.000000	33.219202	0.014640	18.321932

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.659458	0.000097
1.000000	0.642398	0.011418
2.000000	0.626084	0.022139
3.000000	0.610481	0.032291
4.000000	0.595555	0.041900
5.000000	0.581274	0.050993
6.000000	0.567608	0.059595
7.000000	0.554527	0.067729
8.000000	0.542003	0.075419
9.000000	0.530011	0.082686
10.000000	0.518525	0.089550

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11.000000       0.507521       0.096031
12.000000       0.496976       0.102148
13.000000       0.486870       0.107919
14.000000       0.477180       0.113360
15.000000       0.467887       0.118487
16.000000       0.458973       0.123316
17.000000       0.450420       0.127861
18.000000       0.442211       0.132136
19.000000       0.434329       0.136155
20.000000       0.426760       0.139929
21.000000       0.419488       0.143471
22.000000       0.412500       0.146793
23.000000       0.405783       0.149904
24.000000       0.399323       0.152816
25.000000       0.393108       0.155539
26.000000       0.387128       0.158081
27.000000       0.381371       0.160451
28.000000       0.375828       0.162658
29.000000       0.370487       0.164711
30.000000       0.365339       0.166616
31.000000       0.360376       0.168381
32.000000       0.355589       0.170013
33.000000       0.350970       0.171519
34.000000       0.346511       0.172905
35.000000       0.342205       0.174176
36.000000       0.338045       0.175340
37.000000       0.334023       0.176400
38.000000       0.330134       0.177363
39.000000       0.326372       0.178232
40.000000       0.322730       0.179014
41.000000       0.319204       0.179712
42.000000       0.315788       0.180330
43.000000       0.312477       0.180874
44.000000       0.309266       0.181345
45.000000       0.306151       0.181749
46.000000       0.303128       0.182088
47.000000       0.300191       0.182366
48.000000       0.297339       0.182587
49.000000       0.294566       0.182752
50.000000       0.291869       0.182865
51.000000       0.289245       0.182929
52.000000       0.286690       0.182947
53.000000       0.284202       0.182919
54.000000       0.281778       0.182850
55.000000       0.279415       0.182742
56.000000       0.277109       0.182595
57.000000       0.274860       0.182413
58.000000       0.272663       0.182198
59.000000       0.270518       0.181950
60.000000       0.268421       0.181673
61.000000       0.266372       0.181366
62.000000       0.264366       0.181034
63.000000       0.262404       0.180675
64.000000       0.260483       0.180293
65.000000       0.258601       0.179888
66.000000       0.256757       0.179462
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 67.000000       0.254949       0.179016
 68.000000       0.253176       0.178551
 69.000000       0.251436       0.178068
 70.000000       0.249728       0.177568
 71.000000       0.248051       0.177053
 72.000000       0.246403       0.176522
 73.000000       0.244784       0.175978
 74.000000       0.243191       0.175421
 75.000000       0.241625       0.174852
 76.000000       0.240084       0.174271
 77.000000       0.238567       0.173679
 78.000000       0.237074       0.173078
 79.000000       0.235602       0.172467
 80.000000       0.234152       0.171847
 81.000000       0.232724       0.171220
 82.000000       0.231315       0.170585
 83.000000       0.229925       0.169943
 84.000000       0.228554       0.169294
 85.000000       0.227201       0.168640
 86.000000       0.225865       0.167980
 87.000000       0.224546       0.167315
 88.000000       0.223243       0.166645
 89.000000       0.221955       0.165972
 90.000000       0.220683       0.165294
 91.000000       0.219426       0.164613
 92.000000       0.218182       0.163929
 93.000000       0.216952       0.163242
 94.000000       0.215736       0.162553
 95.000000       0.214532       0.161861
 96.000000       0.213341       0.161168
 97.000000       0.212162       0.160473
 98.000000       0.210994       0.159776
 99.000000       0.209838       0.159079
100.000000       0.208693       0.158380
101.000000       0.207559       0.157681
102.000000       0.206435       0.156981
103.000000       0.205321       0.156281
104.000000       0.204217       0.155581
105.000000       0.203123       0.154881
106.000000       0.202039       0.154181
107.000000       0.200963       0.153482
108.000000       0.199896       0.152783
109.000000       0.198838       0.152084
110.000000       0.197789       0.151387
111.000000       0.196748       0.150690
112.000000       0.195715       0.149994
113.000000       0.194690       0.149300
114.000000       0.193672       0.148606
115.000000       0.192663       0.147914
116.000000       0.191660       0.147224
117.000000       0.190665       0.146535
118.000000       0.189677       0.145848
119.000000       0.188696       0.145162
120.000000       0.187722       0.144478
```

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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 2018-2019

Version: 1.1
Date of this report: 20.04.2020 10:40

Study: ECPA-07A
Description: Appendix C ECPA-07 soil A

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	38.6	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	0.003	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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	45.580423	0.007798	0.000000
KOC_EQ	74.243016	0.000678	0.000000
f_NEQ	0.753956	0.038758	0.000000
k_des	0.033224	0.588394	0.476036
DT50_EQ	55.108076	0.002417	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	45.580423	45.565139	45.595707
KOC_EQ	74.243016	74.241688	74.244344
f_NEQ	0.753956	0.677991	0.829922
k_des	0.033224	-1.120029	1.186476
DT50_EQ	55.108076	55.103338	55.112814

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set	
No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	5.774871
Weighted ME (Chi²)	3.467409
Coeff. of Det. (R²)	0.996426
Model efficiency	0.996074
Abs. deviation	28.241191
Quadr. deviation	59.424002
SRMSE	0.066544
STE	0.039548

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R²)	0.975055	0.993620
Model efficiency	0.966962	0.993595
Abs. deviation	28.215638	0.025553
Quadr. deviation	59.423934	0.000067
SRMSE	0.047126	0.032596
STE	0.039573	0.023287

App. sorp. coeff. (mL/g)	
No obs.	19
Coeff. of Det. (R²)	0.959186
Model efficiency	0.942489
Abs. deviation	5.533902
Quadr. deviation	2.700709
SRMSE	0.120927
STE	0.093420

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210000	45.576442	2.633558	0.00043
0.000	48.210000	45.576442	2.633558	0.00043
0.000	48.640000	45.572461	3.067539	0.00042
1.000	47.680000	45.012515	2.667485	0.00044
1.000	47.540000	45.012515	2.527485	0.00044
3.000	44.250000	43.941328	0.308672	0.00051
3.000	44.460000	43.941328	0.518672	0.00051
7.000	42.170000	41.979410	0.190590	0.00056
7.000	42.640000	41.979410	0.660590	0.00055
14.000	38.270000	39.031509	-0.761509	0.00068
14.000	38.600000	39.031509	-0.431509	0.00067
21.000	35.720000	36.541470	-0.821470	0.00078
21.000	35.950000	36.541470	-0.591470	0.00077

30.000	31.440000	33.816153	-2.376153	0.00101
30.000	31.890000	33.816153	-1.926153	0.00098
59.000	25.050000	27.091583	-2.041583	0.00159
59.000	25.030000	27.091583	-2.061583	0.00160
120.000	18.980000	17.631971	1.348029	0.00278
120.000	18.280000	17.631971	0.648029	0.00299

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.088700	0.085948	0.002752	127.10211
0.000	0.088700	0.085948	0.002752	127.10211
0.000	0.089700	0.085927	0.003773	124.28397
1.000	0.079300	0.083070	-0.003770	159.02069
1.000	0.078900	0.083070	-0.004170	160.63715
3.000	0.076900	0.077777	-0.000877	169.10145
3.000	0.077100	0.077777	-0.000677	168.22527
7.000	0.067700	0.068707	-0.001007	218.18388
7.000	0.068300	0.068707	-0.000407	214.36733
14.000	0.055900	0.056727	-0.000827	320.01946
14.000	0.055400	0.056727	-0.001327	325.82205
21.000	0.048700	0.048250	0.000450	421.64026
21.000	0.048500	0.048250	0.000250	425.12488
30.000	0.041100	0.040689	0.000411	591.99271
30.000	0.041100	0.040689	0.000411	591.99271
59.000	0.027700	0.028173	-0.000473	1303.28820
59.000	0.028100	0.028173	-0.000073	1266.44799
120.000	0.017700	0.017176	0.000524	3191.93080
120.000	0.017800	0.017176	0.000624	3156.16715

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	1.435175	1.303258	0.131917	127.10211
0.000000	1.435175	1.303258	0.131917	127.10211
0.000000	1.422520	1.304061	0.118458	124.28397
1.000000	2.012610	1.419058	0.593552	159.02069
1.000000	2.025349	1.419058	0.606290	160.63715
3.000000	1.754226	1.650089	0.104137	169.10145
3.000000	1.766537	1.650089	0.116448	168.22527
7.000000	2.228951	2.110400	0.118552	218.18388
7.000000	2.243045	2.110400	0.132646	214.36733
14.000000	2.846154	2.881103	-0.034950	320.01946
14.000000	2.967509	2.881103	0.086406	325.82205
21.000000	3.334702	3.573802	-0.239100	421.64026
21.000000	3.412371	3.573802	-0.161431	425.12488
30.000000	3.649635	4.311321	-0.661686	591.99271
30.000000	3.759124	4.311321	-0.552197	591.99271
59.000000	5.043321	5.616774	-0.573452	1303.28820
59.000000	4.907473	5.616774	-0.709300	1266.44799
120.000000	6.723164	6.265683	0.457481	3191.93080
120.000000	6.269663	6.265683	0.003980	3156.16715

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	45.576442	0.085948	1.303258

1.000000	45.012515	0.083070	1.419058
2.000000	44.466579	0.080344	1.534989
3.000000	43.937712	0.077760	1.650894
4.000000	43.425040	0.075310	1.766619
5.000000	42.927742	0.072987	1.882010
6.000000	42.445040	0.070784	1.996917
7.000000	41.976200	0.068693	2.111191
8.000000	41.520529	0.066708	2.224686
9.000000	41.077373	0.064824	2.337263
10.000000	40.646113	0.063034	2.448785
11.000000	40.226166	0.061333	2.559124
12.000000	39.816980	0.059716	2.668155
13.000000	39.418035	0.058179	2.775762
14.000000	39.028838	0.056717	2.881835
15.000000	38.648926	0.055325	2.986271
16.000000	38.277859	0.054000	3.088977
17.000000	37.915223	0.052738	3.189865
18.000000	37.560626	0.051535	3.288858
19.000000	37.213698	0.050388	3.385885
20.000000	36.874089	0.049294	3.480884
21.000000	36.541470	0.048250	3.573802
22.000000	36.215528	0.047253	3.664593
23.000000	35.895968	0.046301	3.753218
24.000000	35.582512	0.045391	3.839648
25.000000	35.274895	0.044520	3.923860
26.000000	34.972869	0.043687	4.005837
27.000000	34.676199	0.042889	4.085571
28.000000	34.384661	0.042125	4.163060
29.000000	34.098045	0.041392	4.238307
30.000000	33.816153	0.040689	4.311321
31.000000	33.538795	0.040015	4.382117
32.000000	33.265794	0.039367	4.450715
33.000000	32.996980	0.038744	4.517137
34.000000	32.732195	0.038145	4.581413
35.000000	32.471288	0.037569	4.643575
36.000000	32.214115	0.037014	4.703657
37.000000	31.960542	0.036480	4.761697
38.000000	31.710440	0.035964	4.817737
39.000000	31.463688	0.035467	4.871818
40.000000	31.220172	0.034986	4.923987
41.000000	30.979781	0.034522	4.974289
42.000000	30.742413	0.034074	5.022773
43.000000	30.507970	0.033640	5.069487
44.000000	30.276360	0.033220	5.114480
45.000000	30.047494	0.032813	5.157803
46.000000	29.821289	0.032418	5.199507
47.000000	29.597665	0.032035	5.239642
48.000000	29.376548	0.031663	5.278258
49.000000	29.157866	0.031302	5.315406
50.000000	28.941551	0.030951	5.351136
51.000000	28.727539	0.030610	5.385497
52.000000	28.515769	0.030278	5.418537
53.000000	28.306181	0.029954	5.450306
54.000000	28.098722	0.029639	5.480849
55.000000	27.893337	0.029331	5.510214
56.000000	27.689978	0.029031	5.538445

57.000000	27.488596	0.028738	5.565587
58.000000	27.289145	0.028452	5.591682
59.000000	27.091583	0.028173	5.616774
60.000000	26.895867	0.027899	5.640902
61.000000	26.701959	0.027631	5.664106
62.000000	26.509820	0.027369	5.686426
63.000000	26.319415	0.027113	5.707897
64.000000	26.130709	0.026861	5.728557
65.000000	25.943669	0.026614	5.748440
66.000000	25.758264	0.026373	5.767580
67.000000	25.574464	0.026135	5.786009
68.000000	25.392240	0.025902	5.803759
69.000000	25.211564	0.025673	5.820859
70.000000	25.032410	0.025448	5.837340
71.000000	24.854753	0.025226	5.853229
72.000000	24.678567	0.025009	5.868552
73.000000	24.503830	0.024794	5.883337
74.000000	24.330520	0.024583	5.897606
75.000000	24.158614	0.024376	5.911385
76.000000	23.988091	0.024171	5.924696
77.000000	23.818932	0.023970	5.937561
78.000000	23.651118	0.023771	5.950001
79.000000	23.484629	0.023575	5.962036
80.000000	23.319447	0.023382	5.973685
81.000000	23.155557	0.023192	5.984966
82.000000	22.992939	0.023004	5.995898
83.000000	22.831579	0.022818	6.006496
84.000000	22.671461	0.022635	6.016777
85.000000	22.512570	0.022454	6.026756
86.000000	22.354890	0.022275	6.036448
87.000000	22.198408	0.022098	6.045867
88.000000	22.043109	0.021924	6.055026
89.000000	21.888981	0.021751	6.063938
90.000000	21.736011	0.021580	6.072615
91.000000	21.584185	0.021412	6.081069
92.000000	21.433491	0.021245	6.089310
93.000000	21.283918	0.021080	6.097350
94.000000	21.135453	0.020916	6.105197
95.000000	20.988086	0.020755	6.112863
96.000000	20.841805	0.020595	6.120355
97.000000	20.696599	0.020437	6.127683
98.000000	20.552458	0.020280	6.134855
99.000000	20.409372	0.020125	6.141878
100.000000	20.267330	0.019971	6.148760
101.000000	20.126323	0.019819	6.155509
102.000000	19.986341	0.019668	6.162131
103.000000	19.847374	0.019519	6.168633
104.000000	19.709413	0.019371	6.175020
105.000000	19.572449	0.019225	6.181299
106.000000	19.436474	0.019080	6.187475
107.000000	19.301478	0.018936	6.193553
108.000000	19.167454	0.018793	6.199539
109.000000	19.034391	0.018652	6.205437
110.000000	18.902284	0.018512	6.211252
111.000000	18.771122	0.018373	6.216988
112.000000	18.640899	0.018236	6.222650

113.000000	18.511605	0.018099	6.228240
114.000000	18.383235	0.017964	6.233764
115.000000	18.255780	0.017830	6.239224
116.000000	18.129232	0.017697	6.244624
117.000000	18.003584	0.017565	6.249966
118.000000	17.878830	0.017435	6.255255
119.000000	17.754961	0.017305	6.260493
120.000000	17.631971	0.017176	6.265683

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.455804	0.000065
1.000000	0.441117	0.009107
2.000000	0.427185	0.017575
3.000000	0.413966	0.025501
4.000000	0.401420	0.032915
5.000000	0.389511	0.039847
6.000000	0.378201	0.046325
7.000000	0.367459	0.052375
8.000000	0.357253	0.058022
9.000000	0.347552	0.063288
10.000000	0.338328	0.068195
11.000000	0.329556	0.072765
12.000000	0.321210	0.077016
13.000000	0.313266	0.080968
14.000000	0.305703	0.084637
15.000000	0.298498	0.088040
16.000000	0.291632	0.091193
17.000000	0.285087	0.094110
18.000000	0.278844	0.096804
19.000000	0.272888	0.099290
20.000000	0.267201	0.101578
21.000000	0.261770	0.103682
22.000000	0.256580	0.105610
23.000000	0.251618	0.107375
24.000000	0.246872	0.108986
25.000000	0.242329	0.110451
26.000000	0.237979	0.111780
27.000000	0.233810	0.112980
28.000000	0.229814	0.114059
29.000000	0.225981	0.115025
30.000000	0.222302	0.115885
31.000000	0.218768	0.116644
32.000000	0.215372	0.117309
33.000000	0.212107	0.117885
34.000000	0.208965	0.118379
35.000000	0.205939	0.118794
36.000000	0.203025	0.119136
37.000000	0.200214	0.119410
38.000000	0.197503	0.119620
39.000000	0.194886	0.119769
40.000000	0.192358	0.119861

```
41.000000       0.189914       0.119901
42.000000       0.187550       0.119890
43.000000       0.185262       0.119834
44.000000       0.183045       0.119734
45.000000       0.180897       0.119593
46.000000       0.178813       0.119414
47.000000       0.176791       0.119200
48.000000       0.174827       0.118952
49.000000       0.172918       0.118674
50.000000       0.171062       0.118366
51.000000       0.169256       0.118032
52.000000       0.167497       0.117673
53.000000       0.165783       0.117290
54.000000       0.164113       0.116886
55.000000       0.162483       0.116461
56.000000       0.160892       0.116018
57.000000       0.159339       0.115558
58.000000       0.157821       0.115081
59.000000       0.156336       0.114590
60.000000       0.154884       0.114085
61.000000       0.153462       0.113568
62.000000       0.152069       0.113038
63.000000       0.150705       0.112499
64.000000       0.149367       0.111949
65.000000       0.148055       0.111391
66.000000       0.146767       0.110824
67.000000       0.145503       0.110251
68.000000       0.144261       0.109670
69.000000       0.143041       0.109083
70.000000       0.141841       0.108492
71.000000       0.140661       0.107895
72.000000       0.139500       0.107294
73.000000       0.138357       0.106689
74.000000       0.137232       0.106081
75.000000       0.136124       0.105470
76.000000       0.135032       0.104857
77.000000       0.133955       0.104242
78.000000       0.132894       0.103625
79.000000       0.131847       0.103006
80.000000       0.130814       0.102387
81.000000       0.129795       0.101768
82.000000       0.128789       0.101147
83.000000       0.127796       0.100527
84.000000       0.126814       0.099907
85.000000       0.125845       0.099287
86.000000       0.124887       0.098668
87.000000       0.123941       0.098050
88.000000       0.123005       0.097433
89.000000       0.122080       0.096817
90.000000       0.121164       0.096202
91.000000       0.120259       0.095589
92.000000       0.119364       0.094977
93.000000       0.118478       0.094368
94.000000       0.117601       0.093760
95.000000       0.116733       0.093154
96.000000       0.115874       0.092550
```

97.000000	0.115023	0.091949
98.000000	0.114180	0.091350
99.000000	0.113346	0.090754
100.000000	0.112519	0.090160
101.000000	0.111701	0.089568
102.000000	0.110890	0.088979
103.000000	0.110086	0.088393
104.000000	0.109290	0.087810
105.000000	0.108500	0.087230
106.000000	0.107718	0.086652
107.000000	0.106943	0.086077
108.000000	0.106174	0.085506
109.000000	0.105412	0.084937
110.000000	0.104657	0.084371
111.000000	0.103908	0.083809
112.000000	0.103165	0.083249
113.000000	0.102428	0.082693
114.000000	0.101698	0.082140
115.000000	0.100973	0.081590
116.000000	0.100254	0.081043
117.000000	0.099542	0.080499
118.000000	0.098834	0.079959
119.000000	0.098133	0.079421
120.000000	0.097437	0.078887

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  20.04.2020 10:44

Study: ECPA-07B
Description:   Appendix C ECPA-07 soil B


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   0.067
14      38.29   0.0542
14      39.19   0.056
21      34.53   0.0478
21      35.04   0.0493
30      30.38   0.0408
30      30.76   0.0414
59      21.01   0.025
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 0.003 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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	47.179146	0.005906	0.000000
KOC_EQ	77.278727	0.000579	0.000000
f_NEQ	0.334239	0.051250	0.000000
k_des	0.039860	0.198161	0.420575
DT50_EQ	44.618993	0.003118	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	47.179146	47.167571	47.190722
KOC_EQ	77.278727	77.277592	77.279862
f_NEQ	0.334239	0.233790	0.434688
k_des	0.039860	-0.348535	0.428255
DT50_EQ	44.618993	44.612882	44.625105

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	2.140942
Weighted ME (Chi²)	2.610565
Coeff. of Det. (R²)	0.999484
Model efficiency	0.999384
Abs. deviation	10.740838
Quadr. deviation	9.334498
SRMSE	0.027283
STE	0.015559

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R^2)	0.997764	0.981505
Model efficiency	0.996522	0.981431
Abs. deviation	10.706621	0.034217
Quadr. deviation	9.334317	0.000181
SRMSE	0.019321	0.056423
STE	0.015533	0.032900

	App. sorp. coeff. (mL/g)
No obs.	19
Coeff. of Det. (R^2)	0.927751
Model efficiency	0.913261
Abs. deviation	3.804434
Quadr. deviation	1.598378
SRMSE	0.095723
STE	0.066083

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210000	47.174784	1.035216	0.00043
0.000	47.840000	47.174784	0.665216	0.00044
0.000	47.810000	47.170422	0.639578	0.00044
1.000	46.810000	46.451627	0.358373	0.00046
1.000	48.110000	46.451627	1.658373	0.00043
3.000	45.260000	45.061098	0.198902	0.00049
3.000	45.560000	45.061098	0.498902	0.00048
7.000	42.670000	42.486032	0.183968	0.00055
7.000	43.240000	42.486032	0.753968	0.00053
14.000	38.290000	38.517934	-0.227934	0.00068
14.000	39.190000	38.517934	0.672066	0.00065
21.000	34.530000	35.098177	-0.568177	0.00084
21.000	35.040000	35.098177	-0.058177	0.00081
30.000	30.380000	31.321838	-0.941838	0.00108
30.000	30.760000	31.321838	-0.561838	0.00106
59.000	21.010000	22.235715	-1.225715	0.00227
59.000	21.940000	22.235715	-0.295715	0.00208
120.000	11.260000	11.233668	0.026332	0.00789
120.000	11.370000	11.233668	0.136332	0.00774

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.088700	0.079380	0.009320	127.10211
0.000	0.081500	0.079380	0.002120	150.55139
0.000	0.081800	0.079367	0.002433	149.44913
1.000	0.071400	0.077200	-0.005800	196.15689

1.000	0.070700	0.077200	-0.006500	200.06042
3.000	0.072900	0.073118	-0.000218	188.16764
3.000	0.073400	0.073118	0.000282	185.61278
7.000	0.066200	0.065945	0.000255	228.18339
7.000	0.067000	0.065945	0.001055	222.76676
14.000	0.054200	0.055898	-0.001698	340.40931
14.000	0.056000	0.055898	0.000102	318.87755
21.000	0.047800	0.048216	-0.000416	437.66741
21.000	0.049300	0.048216	0.001084	411.43967
30.000	0.040800	0.040731	0.000069	600.73049
30.000	0.041400	0.040731	0.000669	583.44419
59.000	0.025000	0.026212	-0.001212	1600.00000
59.000	0.026400	0.026212	0.000188	1434.80257
120.000	0.012400	0.012352	0.000048	6503.64204
120.000	0.013100	0.012352	0.000748	5827.16625

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	1.435175	1.943437	-0.508262	127.10211
0.000000	1.869939	1.943437	-0.073498	150.55139
0.000000	1.844743	1.943880	-0.099137	149.44913
1.000000	2.556022	2.017587	0.538435	196.15689
1.000000	2.804809	2.017587	0.787222	200.06042
3.000000	2.208505	2.163384	0.045121	188.16764
3.000000	2.207084	2.163384	0.043700	185.61278
7.000000	2.445619	2.443226	0.002393	228.18339
7.000000	2.453731	2.443226	0.010505	222.76676
14.000000	3.064576	2.891297	0.173279	340.40931
14.000000	2.998214	2.891297	0.106917	318.87755
21.000000	3.223849	3.279858	-0.056009	437.66741
21.000000	3.107505	3.279858	-0.172353	411.43967
30.000000	3.446078	3.690485	-0.244407	600.73049
30.000000	3.429952	3.690485	-0.260533	583.44419
59.000000	4.404000	4.483691	-0.079691	1600.00000
59.000000	4.310606	4.483691	-0.173085	1434.80257
120.000000	5.080645	5.094962	-0.014316	6503.64204
120.000000	4.679389	5.094962	-0.415572	5827.16625

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	47.174784	0.079380	1.943437
1.000000	46.451627	0.077200	2.017587
2.000000	45.747329	0.075114	2.090920
3.000000	45.061098	0.073118	2.163384
4.000000	44.392183	0.071205	2.234931
5.000000	43.739871	0.069374	2.305515
6.000000	43.103484	0.067618	2.375094
7.000000	42.482379	0.065935	2.443631
8.000000	41.875944	0.064320	2.511090
9.000000	41.283598	0.062771	2.577439
10.000000	40.704790	0.061283	2.642650
11.000000	40.138994	0.059854	2.706697
12.000000	39.585712	0.058481	2.769559
13.000000	39.044469	0.057161	2.831216
14.000000	38.514815	0.055891	2.891653

15.000000	37.996320	0.054669	2.950858
16.000000	37.488577	0.053492	3.008821
17.000000	36.991197	0.052359	3.065535
18.000000	36.503810	0.051266	3.120996
19.000000	36.026065	0.050213	3.175202
20.000000	35.557627	0.049197	3.228155
21.000000	35.098177	0.048216	3.279858
22.000000	34.647410	0.047270	3.330317
23.000000	34.205038	0.046355	3.379539
24.000000	33.770784	0.045470	3.427534
25.000000	33.344386	0.044615	3.474313
26.000000	32.925592	0.043788	3.519890
27.000000	32.514164	0.042987	3.564279
28.000000	32.109872	0.042211	3.607496
29.000000	31.712499	0.041460	3.649558
30.000000	31.321838	0.040731	3.690485
31.000000	30.937689	0.040024	3.730295
32.000000	30.559862	0.039338	3.769008
33.000000	30.188177	0.038673	3.806647
34.000000	29.822459	0.038026	3.843232
35.000000	29.462544	0.037397	3.878787
36.000000	29.108272	0.036786	3.913334
37.000000	28.759492	0.036192	3.946896
38.000000	28.416059	0.035614	3.979497
39.000000	28.077832	0.035051	4.011161
40.000000	27.744680	0.034503	4.041911
41.000000	27.416474	0.033968	4.071773
42.000000	27.093092	0.033447	4.100769
43.000000	26.774417	0.032940	4.128924
44.000000	26.460334	0.032444	4.156262
45.000000	26.150737	0.031960	4.182807
46.000000	25.845522	0.031488	4.208581
47.000000	25.544587	0.031027	4.233609
48.000000	25.247839	0.030576	4.257912
49.000000	24.955183	0.030136	4.281515
50.000000	24.666531	0.029705	4.304439
51.000000	24.381798	0.029283	4.326706
52.000000	24.100901	0.028871	4.348338
53.000000	23.823761	0.028467	4.369355
54.000000	23.550302	0.028072	4.389779
55.000000	23.280449	0.027685	4.409630
56.000000	23.014131	0.027306	4.428928
57.000000	22.751280	0.026934	4.447691
58.000000	22.491830	0.026569	4.465939
59.000000	22.235715	0.026212	4.483691
60.000000	21.982875	0.025861	4.500963
61.000000	21.733249	0.025517	4.517775
62.000000	21.486778	0.025179	4.534141
63.000000	21.243408	0.024848	4.550080
64.000000	21.003084	0.024522	4.565606
65.000000	20.765752	0.024202	4.580736
66.000000	20.531362	0.023888	4.595484
67.000000	20.299864	0.023579	4.609865
68.000000	20.071210	0.023276	4.623894
69.000000	19.845352	0.022977	4.637583
70.000000	19.622247	0.022684	4.650946

71.000000	19.401849	0.022395	4.663996
72.000000	19.184116	0.022111	4.676745
73.000000	18.969006	0.021832	4.689205
74.000000	18.756478	0.021557	4.701388
75.000000	18.546493	0.021287	4.713305
76.000000	18.339013	0.021020	4.724966
77.000000	18.133999	0.020758	4.736382
78.000000	17.931415	0.020500	4.747562
79.000000	17.731225	0.020246	4.758518
80.000000	17.533395	0.019996	4.769257
81.000000	17.337891	0.019749	4.779789
82.000000	17.144679	0.019506	4.790122
83.000000	16.953727	0.019266	4.800264
84.000000	16.765003	0.019030	4.810225
85.000000	16.578476	0.018798	4.820011
86.000000	16.394116	0.018568	4.829629
87.000000	16.211894	0.018342	4.839087
88.000000	16.031780	0.018120	4.848392
89.000000	15.853745	0.017900	4.857551
90.000000	15.677763	0.017683	4.866569
91.000000	15.503805	0.017469	4.875452
92.000000	15.331845	0.017259	4.884207
93.000000	15.161857	0.017051	4.892840
94.000000	14.993815	0.016846	4.901354
95.000000	14.827695	0.016643	4.909757
96.000000	14.663470	0.016444	4.918052
97.000000	14.501117	0.016247	4.926245
98.000000	14.340613	0.016052	4.934340
99.000000	14.181933	0.015860	4.942341
100.000000	14.025055	0.015671	4.950254
101.000000	13.869956	0.015484	4.958081
102.000000	13.716614	0.015300	4.965826
103.000000	13.565007	0.015118	4.973494
104.000000	13.415114	0.014938	4.981089
105.000000	13.266913	0.014761	4.988612
106.000000	13.120385	0.014586	4.996069
107.000000	12.975508	0.014413	5.003461
108.000000	12.832262	0.014242	5.010792
109.000000	12.690628	0.014073	5.018066
110.000000	12.550586	0.013907	5.025284
111.000000	12.412118	0.013743	5.032449
112.000000	12.275203	0.013580	5.039564
113.000000	12.139825	0.013420	5.046632
114.000000	12.005963	0.013262	5.053655
115.000000	11.873601	0.013105	5.060634
116.000000	11.742721	0.012951	5.067573
117.000000	11.613304	0.012799	5.074473
118.000000	11.485334	0.012648	5.081337
119.000000	11.358795	0.012499	5.088166
120.000000	11.233668	0.012352	5.094962

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.471791	0.000032
1.000000	0.459387	0.005202
2.000000	0.447505	0.010038
3.000000	0.436119	0.014558
4.000000	0.425205	0.018781
5.000000	0.414738	0.022722
6.000000	0.404696	0.026398
7.000000	0.395058	0.029822
8.000000	0.385803	0.033010
9.000000	0.376913	0.035974
10.000000	0.368370	0.038728
11.000000	0.360156	0.041282
12.000000	0.352255	0.043648
13.000000	0.344652	0.045837
14.000000	0.337332	0.047859
15.000000	0.330281	0.049724
16.000000	0.323486	0.051439
17.000000	0.316936	0.053015
18.000000	0.310617	0.054458
19.000000	0.304519	0.055777
20.000000	0.298632	0.056979
21.000000	0.292945	0.058070
22.000000	0.287450	0.059057
23.000000	0.282136	0.059946
24.000000	0.276995	0.060743
25.000000	0.272020	0.061453
26.000000	0.267203	0.062081
27.000000	0.262536	0.062633
28.000000	0.258012	0.063113
29.000000	0.253626	0.063525
30.000000	0.249371	0.063873
31.000000	0.245240	0.064161
32.000000	0.241229	0.064393
33.000000	0.237332	0.064572
34.000000	0.233544	0.064702
35.000000	0.229861	0.064786
36.000000	0.226277	0.064826
37.000000	0.222789	0.064826
38.000000	0.219393	0.064788
39.000000	0.216084	0.064714
40.000000	0.212859	0.064606
41.000000	0.209715	0.064468
42.000000	0.206648	0.064301
43.000000	0.203655	0.064107
44.000000	0.200733	0.063887
45.000000	0.197880	0.063644
46.000000	0.195092	0.063380
47.000000	0.192367	0.063095
48.000000	0.189703	0.062791
49.000000	0.187097	0.062470
50.000000	0.184547	0.062133
51.000000	0.182051	0.061781
52.000000	0.179607	0.061416
53.000000	0.177214	0.061038
54.000000	0.174869	0.060648

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 55.000000       0.172570       0.060248
 56.000000       0.170317       0.059838
 57.000000       0.168106       0.059419
 58.000000       0.165938       0.058993
 59.000000       0.163811       0.058559
 60.000000       0.161723       0.058118
 61.000000       0.159672       0.057672
 62.000000       0.157659       0.057221
 63.000000       0.155681       0.056765
 64.000000       0.153738       0.056305
 65.000000       0.151828       0.055841
 66.000000       0.149950       0.055375
 67.000000       0.148104       0.054905
 68.000000       0.146289       0.054434
 69.000000       0.144503       0.053961
 70.000000       0.142746       0.053487
 71.000000       0.141016       0.053012
 72.000000       0.139315       0.052537
 73.000000       0.137639       0.052061
 74.000000       0.135990       0.051585
 75.000000       0.134365       0.051109
 76.000000       0.132765       0.050634
 77.000000       0.131189       0.050160
 78.000000       0.129637       0.049687
 79.000000       0.128107       0.049215
 80.000000       0.126599       0.048744
 81.000000       0.125112       0.048275
 82.000000       0.123647       0.047808
 83.000000       0.122203       0.047343
 84.000000       0.120778       0.046880
 85.000000       0.119374       0.046419
 86.000000       0.117988       0.045961
 87.000000       0.116622       0.045505
 88.000000       0.115274       0.045052
 89.000000       0.113944       0.044601
 90.000000       0.112632       0.044153
 91.000000       0.111337       0.043708
 92.000000       0.110060       0.043266
 93.000000       0.108799       0.042827
 94.000000       0.107554       0.042392
 95.000000       0.106325       0.041959
 96.000000       0.105113       0.041529
 97.000000       0.103915       0.041103
 98.000000       0.102733       0.040680
 99.000000       0.101566       0.040260
100.000000       0.100413       0.039844
101.000000       0.099275       0.039431
102.000000       0.098151       0.039022
103.000000       0.097041       0.038615
104.000000       0.095945       0.038213
105.000000       0.094862       0.037814
106.000000       0.093792       0.037418
107.000000       0.092736       0.037026
108.000000       0.091692       0.036637
109.000000       0.090661       0.036252
110.000000       0.089642       0.035870
```

111.000000	0.088635	0.035492
112.000000	0.087641	0.035117
113.000000	0.086658	0.034746
114.000000	0.085687	0.034378
115.000000	0.084728	0.034014
116.000000	0.083780	0.033653
117.000000	0.082843	0.033296
118.000000	0.081917	0.032942
119.000000	0.081002	0.032592
120.000000	0.080098	0.032245

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  20.04.2020 12:24

Study: ECPA-07C
Description:   Appendix C ECPA-07 soil C


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      31.8    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 0.003 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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	47.099907	0.010193	0.000000
KOC_EQ	98.805982	0.000759	0.000000
f_NEQ	0.748943	0.038696	0.000000
k_des	0.041468	0.407507	0.460074
DT50_EQ	77.022882	0.001043	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	47.099907	47.079929	47.119885
KOC_EQ	98.805982	98.804495	98.807468
f_NEQ	0.748943	0.673098	0.824788
k_des	0.041468	-0.757246	0.840182
DT50_EQ	77.022882	77.020838	77.024926

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	3.313734
Weighted ME (Chi²)	3.791934
Coeff. of Det. (R²)	0.998762
Model efficiency	0.998746
Abs. deviation	17.316875
Quadr. deviation	21.003368
SRMSE	0.036482
STE	0.022362

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R^2)	0.980910	0.901315
Model efficiency	0.979814	0.896923
Abs. deviation	17.267270	0.049605
Quadr. deviation	21.002718	0.000650
SRMSE	0.025824	0.131084
STE	0.022322	0.058510

	App. sorp. coeff. (mL/g)
No obs.	19
Coeff. of Det. (R^2)	0.924004
Model efficiency	0.922846
Abs. deviation	9.699970
Quadr. deviation	9.475701
SRMSE	0.115091
STE	0.083201

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210000	47.097384	1.112616	0.00043
0.000	47.790000	47.097384	0.692616	0.00044
0.000	47.830000	47.094861	0.735139	0.00044
1.000	48.660000	46.681250	1.978750	0.00042
1.000	48.690000	46.681250	2.008750	0.00042
3.000	46.080000	45.892089	0.187911	0.00047
3.000	46.310000	45.892089	0.417911	0.00047
7.000	44.390000	44.463558	-0.073558	0.00051
7.000	44.610000	44.463558	0.146442	0.00050
14.000	41.360000	42.318983	-0.958983	0.00058
14.000	41.320000	42.318983	-0.998983	0.00059
21.000	40.110000	40.487405	-0.377405	0.00062
21.000	39.780000	40.487405	-0.707405	0.00063
30.000	37.220000	38.429540	-1.209540	0.00072
30.000	37.310000	38.429540	-1.119540	0.00072
59.000	31.630000	32.963818	-1.333818	0.00100
59.000	31.800000	32.963818	-1.163818	0.00099
120.000	25.390000	24.197957	1.192043	0.00155
120.000	25.050000	24.197957	0.852043	0.00159

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.088700	0.064529	0.024171	127.10211
0.000	0.066100	0.064529	0.001571	228.87433
0.000	0.065700	0.064514	0.001186	231.66971
1.000	0.059500	0.062067	-0.002567	282.46593

1.000	0.056200	0.062067	-0.005867	316.61200
3.000	0.054900	0.057629	-0.002729	331.78390
3.000	0.056100	0.057629	-0.001529	317.74175
7.000	0.049400	0.050403	-0.001003	409.77561
7.000	0.048700	0.050403	-0.001703	421.64026
14.000	0.041100	0.041578	-0.000478	591.99271
14.000	0.041200	0.041578	-0.000378	589.12244
21.000	0.036100	0.035902	0.000198	767.33604
21.000	0.036900	0.035902	0.000998	734.42469
30.000	0.032900	0.031264	0.001636	923.86434
30.000	0.032600	0.031264	0.001336	940.94622
59.000	0.023700	0.024178	-0.000478	1780.34147
59.000	0.023800	0.024178	-0.000378	1765.41205
120.000	0.016400	0.017065	-0.000665	3718.02499
120.000	0.017800	0.017065	0.000735	3156.16715

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	1.435175	3.299014	-1.863839	127.10211
0.000000	3.229955	3.299014	-0.069059	228.87433
0.000000	3.280061	3.300340	-0.020279	231.66971
1.000000	4.178151	3.521513	0.656638	282.46593
1.000000	4.663701	3.521513	1.142188	316.61200
3.000000	4.393443	3.963717	0.429726	331.78390
3.000000	4.254902	3.963717	0.291185	317.74175
7.000000	4.985830	4.821966	0.163864	409.77561
7.000000	5.160164	4.821966	0.338198	421.64026
14.000000	6.063260	6.178708	-0.115447	591.99271
14.000000	6.029126	6.178708	-0.149582	589.12244
21.000000	7.110803	7.277510	-0.166707	767.33604
21.000000	6.780488	7.277510	-0.497022	734.42469
30.000000	7.313070	8.292225	-0.979155	923.86434
30.000000	7.444785	8.292225	-0.847440	940.94622
59.000000	9.345992	9.634151	-0.288160	1780.34147
59.000000	9.361345	9.634151	-0.272807	1765.41205
120.000000	11.481707	10.180249	1.301459	3718.02499
120.000000	10.073034	10.180249	-0.107215	3156.16715

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	47.097384	0.064529	3.299014
1.000000	46.681250	0.062067	3.521513
2.000000	46.279805	0.059771	3.743251
3.000000	45.892089	0.057629	3.963717
4.000000	45.517208	0.055631	4.182414
5.000000	45.154332	0.053765	4.398863
6.000000	44.802688	0.052022	4.612606
7.000000	44.461557	0.050394	4.823209
8.000000	44.130270	0.048872	5.030270
9.000000	43.808204	0.047447	5.233416
10.000000	43.494783	0.046115	5.432306
11.000000	43.189466	0.044867	5.626636
12.000000	42.891754	0.043697	5.816137
13.000000	42.601181	0.042601	6.000577
14.000000	42.317312	0.041572	6.179758

15.000000	42.039746	0.040606	6.353521
16.000000	41.768106	0.039699	6.521739
17.000000	41.502044	0.038845	6.684320
18.000000	41.241235	0.038043	6.841204
19.000000	40.985376	0.037287	6.992360
20.000000	40.734187	0.036574	7.137788
21.000000	40.487405	0.035902	7.277510
22.000000	40.244787	0.035268	7.411576
23.000000	40.006105	0.034668	7.540054
24.000000	39.771149	0.034101	7.663033
25.000000	39.539723	0.033565	7.780618
26.000000	39.311642	0.033056	7.892929
27.000000	39.086737	0.032573	8.000099
28.000000	38.864848	0.032115	8.102269
29.000000	38.645828	0.031679	8.199592
30.000000	38.429540	0.031264	8.292225
31.000000	38.215853	0.030869	8.380331
32.000000	38.004650	0.030492	8.464076
33.000000	37.795818	0.030133	8.543629
34.000000	37.589254	0.029788	8.619158
35.000000	37.384860	0.029459	8.690834
36.000000	37.182546	0.029144	8.758824
37.000000	36.982227	0.028841	8.823294
38.000000	36.783826	0.028550	8.884408
39.000000	36.587268	0.028270	8.942324
40.000000	36.392485	0.028001	8.997200
41.000000	36.199412	0.027742	9.049187
42.000000	36.007991	0.027491	9.098432
43.000000	35.818165	0.027249	9.145078
44.000000	35.629881	0.027015	9.189261
45.000000	35.443092	0.026789	9.231115
46.000000	35.257750	0.026569	9.270766
47.000000	35.073814	0.026356	9.308335
48.000000	34.891243	0.026148	9.343940
49.000000	34.710000	0.025947	9.377691
50.000000	34.530049	0.025751	9.409693
51.000000	34.351358	0.025560	9.440049
52.000000	34.173895	0.025373	9.468854
53.000000	33.997632	0.025191	9.496199
54.000000	33.822540	0.025013	9.522171
55.000000	33.648595	0.024839	9.546852
56.000000	33.475773	0.024669	9.570318
57.000000	33.304050	0.024502	9.592645
58.000000	33.133405	0.024339	9.613901
59.000000	32.963818	0.024178	9.634151
60.000000	32.795270	0.024021	9.653458
61.000000	32.627742	0.023866	9.671880
62.000000	32.461219	0.023713	9.689472
63.000000	32.295684	0.023563	9.706286
64.000000	32.131121	0.023416	9.722370
65.000000	31.967516	0.023271	9.737770
66.000000	31.804856	0.023127	9.752530
67.000000	31.643128	0.022986	9.766689
68.000000	31.482319	0.022847	9.780287
69.000000	31.322417	0.022709	9.793359
70.000000	31.163411	0.022573	9.805939

71.000000	31.005292	0.022439	9.818057
72.000000	30.848047	0.022306	9.829745
73.000000	30.691669	0.022175	9.841029
74.000000	30.536147	0.022045	9.851936
75.000000	30.381473	0.021917	9.862489
76.000000	30.227637	0.021790	9.872713
77.000000	30.074633	0.021664	9.882628
78.000000	29.922451	0.021540	9.892255
79.000000	29.771085	0.021416	9.901612
80.000000	29.620527	0.021294	9.910718
81.000000	29.470770	0.021173	9.919588
82.000000	29.321808	0.021053	9.928238
83.000000	29.173633	0.020934	9.936682
84.000000	29.026239	0.020816	9.944935
85.000000	28.879620	0.020698	9.953009
86.000000	28.733771	0.020582	9.960915
87.000000	28.588685	0.020467	9.968665
88.000000	28.444357	0.020353	9.976270
89.000000	28.300781	0.020239	9.983739
90.000000	28.157953	0.020126	9.991080
91.000000	28.015865	0.020014	9.998304
92.000000	27.874515	0.019903	10.005416
93.000000	27.733896	0.019793	10.012426
94.000000	27.594004	0.019683	10.019340
95.000000	27.454834	0.019575	10.026165
96.000000	27.316382	0.019467	10.032906
97.000000	27.178643	0.019359	10.039570
98.000000	27.041611	0.019253	10.046161
99.000000	26.905284	0.019147	10.052685
100.000000	26.769657	0.019041	10.059146
101.000000	26.634725	0.018937	10.065549
102.000000	26.500485	0.018833	10.071898
103.000000	26.366932	0.018730	10.078196
104.000000	26.234062	0.018627	10.084448
105.000000	26.101871	0.018525	10.090655
106.000000	25.970355	0.018423	10.096823
107.000000	25.839511	0.018323	10.102953
108.000000	25.709335	0.018222	10.109048
109.000000	25.579822	0.018123	10.115110
110.000000	25.450969	0.018024	10.121143
111.000000	25.322773	0.017925	10.127148
112.000000	25.195230	0.017828	10.133128
113.000000	25.068335	0.017730	10.139083
114.000000	24.942087	0.017634	10.145017
115.000000	24.816480	0.017538	10.150931
116.000000	24.691512	0.017442	10.156826
117.000000	24.567179	0.017347	10.162704
118.000000	24.443478	0.017252	10.168566
119.000000	24.320405	0.017159	10.174414
120.000000	24.197957	0.017065	10.180249

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.470999	0.000079
1.000000	0.454113	0.012796
2.000000	0.438334	0.024555
3.000000	0.423584	0.035422
4.000000	0.409791	0.045461
5.000000	0.396888	0.054729
6.000000	0.384814	0.063282
7.000000	0.373511	0.071170
8.000000	0.362924	0.078440
9.000000	0.353003	0.085136
10.000000	0.343703	0.091298
11.000000	0.334980	0.096965
12.000000	0.326793	0.102171
13.000000	0.319106	0.106950
14.000000	0.311883	0.111331
15.000000	0.305093	0.115344
16.000000	0.298705	0.119013
17.000000	0.292690	0.122365
18.000000	0.287024	0.125421
19.000000	0.281682	0.128202
20.000000	0.276642	0.130729
21.000000	0.271882	0.133019
22.000000	0.267384	0.135090
23.000000	0.263129	0.136957
24.000000	0.259100	0.138635
25.000000	0.255282	0.140137
26.000000	0.251660	0.141477
27.000000	0.248221	0.142666
28.000000	0.244953	0.143715
29.000000	0.241843	0.144633
30.000000	0.238881	0.145432
31.000000	0.236057	0.146118
32.000000	0.233361	0.146702
33.000000	0.230784	0.147189
34.000000	0.228320	0.147587
35.000000	0.225959	0.147904
36.000000	0.223695	0.148144
37.000000	0.221522	0.148313
38.000000	0.219433	0.148417
39.000000	0.217424	0.148461
40.000000	0.215488	0.148449
41.000000	0.213620	0.148385
42.000000	0.211817	0.148273
43.000000	0.210075	0.148117
44.000000	0.208388	0.147921
45.000000	0.206754	0.147687
46.000000	0.205169	0.147418
47.000000	0.203630	0.147118
48.000000	0.202134	0.146787
49.000000	0.200678	0.146430
50.000000	0.199261	0.146048
51.000000	0.197879	0.145643
52.000000	0.196530	0.145217
53.000000	0.195213	0.144771
54.000000	0.193925	0.144308

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 55.000000       0.192664       0.143829
 56.000000       0.191430       0.143335
 57.000000       0.190220       0.142827
 58.000000       0.189034       0.142307
 59.000000       0.187869       0.141776
 60.000000       0.186724       0.141235
 61.000000       0.185600       0.140684
 62.000000       0.184493       0.140126
 63.000000       0.183404       0.139559
 64.000000       0.182331       0.138986
 65.000000       0.181274       0.138407
 66.000000       0.180232       0.137823
 67.000000       0.179204       0.137234
 68.000000       0.178189       0.136640
 69.000000       0.177187       0.136044
 70.000000       0.176197       0.135443
 71.000000       0.175218       0.134841
 72.000000       0.174251       0.134236
 73.000000       0.173294       0.133629
 74.000000       0.172347       0.133020
 75.000000       0.171410       0.132410
 76.000000       0.170482       0.131800
 77.000000       0.169563       0.131188
 78.000000       0.168653       0.130577
 79.000000       0.167751       0.129965
 80.000000       0.166857       0.129353
 81.000000       0.165971       0.128742
 82.000000       0.165092       0.128131
 83.000000       0.164220       0.127521
 84.000000       0.163355       0.126912
 85.000000       0.162497       0.126304
 86.000000       0.161646       0.125697
 87.000000       0.160801       0.125091
 88.000000       0.159962       0.124487
 89.000000       0.159129       0.123884
 90.000000       0.158302       0.123283
 91.000000       0.157480       0.122683
 92.000000       0.156664       0.122086
 93.000000       0.155854       0.121490
 94.000000       0.155049       0.120896
 95.000000       0.154249       0.120304
 96.000000       0.153454       0.119714
 97.000000       0.152665       0.119126
 98.000000       0.151880       0.118541
 99.000000       0.151100       0.117957
100.000000       0.150325       0.117376
101.000000       0.149554       0.116797
102.000000       0.148788       0.116221
103.000000       0.148027       0.115647
104.000000       0.147270       0.115075
105.000000       0.146517       0.114506
106.000000       0.145769       0.113939
107.000000       0.145025       0.113374
108.000000       0.144286       0.112812
109.000000       0.143550       0.112253
110.000000       0.142819       0.111696
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111.000000	0.142091	0.111141
112.000000	0.141368	0.110589
113.000000	0.140648	0.110039
114.000000	0.139933	0.109492
115.000000	0.139221	0.108948
116.000000	0.138514	0.108406
117.000000	0.137810	0.107866
118.000000	0.137110	0.107329
119.000000	0.136413	0.106795
120.000000	0.135721	0.106263

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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

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SorpKinAnalysis - Two-site aged sorption model
Kinetic sorption analysis (Leistra et al. 2001)
developed by Judith Klein and Michael Klein 2018-2019


Version:       1.1
Date of this report:  20.04.2020 12:26

Study: ECPA-07D
Description:   Appendix C ECPA-07 soil D


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       44.2    0.0503
1       45.67   0.0491
3       45.37   0.0487
3       44.87   0.049
7       43.21   0.0436
7       43.2    0.0437
14      37.97   0.0365
14      38.3    0.0364
21      34.26   0.0314
21      33.96   0.0321
30      31.69   0.0269
30      31.73   0.027
59      22.9    0.017
59      23.42   0.0168
120     14.31   0.0089
120     14.5    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 0.003 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)

Parameter uncertainty

Parameter	Value	Standard Error	Prob > t
M_0	46.087128	0.009917	0.000000
KOC_EQ	64.679782	0.001136	0.000000
f_NEQ	0.515617	0.037446	0.000000
k_des	0.031589	0.394140	0.468044
DT50_EQ	48.064929	0.002521	0.000000

Parameter	Value	Lower Bound	Upper Bound
M_0	46.087128	46.067690	46.106566
KOC_EQ	64.679782	64.677556	64.682009
f_NEQ	0.515617	0.442223	0.589012
k_des	0.031589	-0.740924	0.804103
DT50_EQ	48.064929	48.059987	48.069870

Upper and lower bounds of parameter is not taken into account in the calculation of 95% confidence intervals.

EVALUATION

Complete Data Set

No obs.	38
No act. param.	5
Deg. of Freedom	13
Model error (Chi²)	3.150422
Weighted ME (Chi²)	4.228196
Coeff. of Det. (R²)	0.998803
Model efficiency	0.998737
Abs. deviation	15.909901
Quadr. deviation	18.529749
SRMSE	0.038344
STE	0.022990

	Total mass (µg)	Conc liq. phase (µg/mL)
No obs.	19	19
Coeff. of Det. (R^2)	0.992497	0.829591
Model efficiency	0.991281	0.820550
Abs. deviation	15.859596	0.050305
Quadr. deviation	18.528570	0.001179
SRMSE	0.027141	0.207001
STE	0.022941	0.069568

	App. sorp. coeff. (mL/g)
No obs.	19
Coeff. of Det. (R^2)	0.904743
Model efficiency	0.903396
Abs. deviation	10.164844
Quadr. deviation	12.366858
SRMSE	0.118984
STE	0.078901

MEASURED VERSUS PREDICTED VALUES (%)

Total mass (µg)

Time	Measured	Predicted	Residuals	Weight
0.000	48.210000	46.081589	2.128411	0.00043
0.000	46.970000	46.081589	0.888411	0.00045
0.000	46.570000	46.076052	0.493948	0.00046
1.000	44.200000	45.426556	-1.226556	0.00051
1.000	45.670000	45.426556	0.243444	0.00048
3.000	45.370000	44.171094	1.198906	0.00049
3.000	44.870000	44.171094	0.698906	0.00050
7.000	43.210000	41.862037	1.347963	0.00054
7.000	43.200000	41.862037	1.337963	0.00054
14.000	37.970000	38.335479	-0.365479	0.00069
14.000	38.300000	38.335479	-0.035479	0.00068
21.000	34.260000	35.337234	-1.077234	0.00085
21.000	33.960000	35.337234	-1.377234	0.00087
30.000	31.690000	32.052846	-0.362846	0.00100
30.000	31.730000	32.052846	-0.322846	0.00099
59.000	22.900000	24.161227	-1.261227	0.00191
59.000	23.420000	24.161227	-0.741227	0.00182
120.000	14.310000	14.029243	0.280757	0.00488
120.000	14.500000	14.029243	0.470757	0.00476

Conc liq. phase (µg/mL)

Time	Measured	Predicted	Residuals	Weight
0.000	0.088700	0.054847	0.033853	127.10211
0.000	0.053700	0.054847	-0.001147	346.77791
0.000	0.054400	0.054832	-0.000432	337.91090
1.000	0.050300	0.053171	-0.002871	395.24286

1.000	0.049100	0.053171	-0.004071	414.79835
3.000	0.048700	0.050045	-0.001345	421.64026
3.000	0.049000	0.050045	-0.001045	416.49313
7.000	0.043600	0.044599	-0.000999	526.05000
7.000	0.043700	0.044599	-0.000899	523.64520
14.000	0.036500	0.037091	-0.000591	750.60987
14.000	0.036400	0.037091	-0.000691	754.73977
21.000	0.031400	0.031517	-0.000117	1014.23993
21.000	0.032100	0.031517	0.000583	970.48748
30.000	0.026900	0.026274	0.000626	1381.95990
30.000	0.027000	0.026274	0.000726	1371.74211
59.000	0.017000	0.016921	0.000079	3460.20761
59.000	0.016800	0.016921	-0.000121	3543.08390
120.000	0.008900	0.008847	0.000053	12624.66860
120.000	0.008900	0.008847	0.000053	12624.66860

App. sorp. coeff. (mL/g)

Time	Measured	Predicted	Residuals	Weight
0.000000	1.435175	4.402922	-2.967747	127.10211
0.000000	4.746741	4.402922	0.343819	346.77791
0.000000	4.560662	4.404101	0.156560	337.91090
1.000000	4.787276	4.544484	0.242793	395.24286
1.000000	5.301426	4.544484	0.756942	414.79835
3.000000	5.316222	4.827335	0.488887	421.64026
3.000000	5.157143	4.827335	0.329808	416.49313
7.000000	5.910550	5.387324	0.523227	526.05000
7.000000	5.885584	5.387324	0.498260	523.64520
14.000000	6.402740	6.336594	0.066146	750.60987
14.000000	6.521978	6.336594	0.185384	754.73977
21.000000	6.910828	7.213221	-0.302392	1014.23993
21.000000	6.579439	7.213221	-0.633781	970.48748
30.000000	7.780669	8.200667	-0.419998	1381.95990
30.000000	7.751852	8.200667	-0.448815	1371.74211
59.000000	9.470588	10.279854	-0.809266	3460.20761
59.000000	9.940476	10.279854	-0.339378	3543.08390
120.000000	12.078652	11.859573	0.219079	12624.66860
120.000000	12.292135	11.859573	0.432562	12624.66860

Time (days)	Total mass (µg)	Conc liq. phase (µg/mL)	App. sorp. coeff. (mL/g)
0.000000	46.081589	0.054847	4.402922
1.000000	45.426556	0.053171	4.544484
2.000000	44.789991	0.051572	4.685997
3.000000	44.171094	0.050045	4.827335
4.000000	43.569100	0.048587	4.968375
5.000000	42.983286	0.047193	5.108993
6.000000	42.412960	0.045862	5.249069
7.000000	41.857467	0.044589	5.388483
8.000000	41.316182	0.043372	5.527120
9.000000	40.788509	0.042208	5.664868
10.000000	40.273885	0.041094	5.801617
11.000000	39.771769	0.040027	5.937263
12.000000	39.281651	0.039006	6.071705
13.000000	38.803042	0.038028	6.204845
14.000000	38.335479	0.037091	6.336594

15.000000	37.878519	0.036193	6.466864
16.000000	37.431742	0.035331	6.595573
17.000000	36.994747	0.034505	6.722644
18.000000	36.567154	0.033712	6.848008
19.000000	36.148598	0.032951	6.971598
20.000000	35.738735	0.032220	7.093353
21.000000	35.337234	0.031517	7.213221
22.000000	34.943782	0.030842	7.331150
23.000000	34.558081	0.030192	7.447097
24.000000	34.179844	0.029568	7.561025
25.000000	33.808801	0.028966	7.672899
26.000000	33.444693	0.028387	7.782693
27.000000	33.087273	0.027830	7.890382
28.000000	32.736306	0.027292	7.995949
29.000000	32.391568	0.026774	8.099380
30.000000	32.052846	0.026274	8.200667
31.000000	31.719935	0.025791	8.299805
32.000000	31.392641	0.025325	8.396794
33.000000	31.070778	0.024876	8.491638
34.000000	30.754170	0.024441	8.584343
35.000000	30.442647	0.024020	8.674920
36.000000	30.136048	0.023613	8.763385
37.000000	29.834218	0.023220	8.849753
38.000000	29.537012	0.022839	8.934045
39.000000	29.244288	0.022469	9.016284
40.000000	28.955912	0.022112	9.096495
41.000000	28.671756	0.021765	9.174704
42.000000	28.391697	0.021428	9.250942
43.000000	28.115618	0.021101	9.325240
44.000000	27.843407	0.020784	9.397630
45.000000	27.574957	0.020476	9.468184
46.000000	27.310164	0.020176	9.536863
47.000000	27.048932	0.019885	9.603740
48.000000	26.791165	0.019602	9.668853
49.000000	26.536774	0.019326	9.732239
50.000000	26.285673	0.019057	9.793939
51.000000	26.037779	0.018796	9.853990
52.000000	25.793012	0.018541	9.912433
53.000000	25.551298	0.018292	9.969308
54.000000	25.312563	0.018050	10.024654
55.000000	25.076737	0.017813	10.078512
56.000000	24.843754	0.017583	10.130921
57.000000	24.613549	0.017357	10.181921
58.000000	24.386060	0.017137	10.231553
59.000000	24.161227	0.016921	10.279854
60.000000	23.938995	0.016710	10.326865
61.000000	23.719308	0.016504	10.372623
62.000000	23.502113	0.016303	10.417166
63.000000	23.287360	0.016105	10.460532
64.000000	23.074999	0.015912	10.502757
65.000000	22.864984	0.015723	10.543878
66.000000	22.657269	0.015537	10.583930
67.000000	22.451811	0.015355	10.622947
68.000000	22.248568	0.015177	10.660965
69.000000	22.047499	0.015001	10.698016
70.000000	21.848565	0.014830	10.734132

71.000000	21.651728	0.014661	10.769347
72.000000	21.456951	0.014495	10.803690
73.000000	21.264200	0.014333	10.837193
74.000000	21.073440	0.014173	10.869884
75.000000	20.884638	0.014016	10.901792
76.000000	20.697763	0.013862	10.932946
77.000000	20.512783	0.013710	10.963373
78.000000	20.329668	0.013560	10.993098
79.000000	20.148390	0.013413	11.022149
80.000000	19.968921	0.013269	11.050549
81.000000	19.791233	0.013127	11.078322
82.000000	19.615299	0.012987	11.105493
83.000000	19.441095	0.012849	11.132083
84.000000	19.268596	0.012713	11.158116
85.000000	19.097776	0.012579	11.183611
86.000000	18.928613	0.012447	11.208591
87.000000	18.761084	0.012317	11.233073
88.000000	18.595167	0.012189	11.257079
89.000000	18.430839	0.012062	11.280626
90.000000	18.268080	0.011938	11.303733
91.000000	18.106870	0.011815	11.326416
92.000000	17.947188	0.011694	11.348693
93.000000	17.789014	0.011574	11.370580
94.000000	17.632331	0.011456	11.392092
95.000000	17.477119	0.011340	11.413245
96.000000	17.323359	0.011225	11.434052
97.000000	17.171036	0.011112	11.454529
98.000000	17.020130	0.011000	11.474688
99.000000	16.870626	0.010889	11.494543
100.000000	16.722506	0.010780	11.514105
101.000000	16.575755	0.010672	11.533388
102.000000	16.430356	0.010565	11.552402
103.000000	16.286295	0.010460	11.571159
104.000000	16.143556	0.010356	11.589668
105.000000	16.002124	0.010253	11.607940
106.000000	15.861985	0.010152	11.625987
107.000000	15.723124	0.010051	11.643818
108.000000	15.585527	0.009952	11.661442
109.000000	15.449181	0.009854	11.678867
110.000000	15.314071	0.009757	11.696104
111.000000	15.180186	0.009662	11.713158
112.000000	15.047512	0.009567	11.730040
113.000000	14.916035	0.009473	11.746756
114.000000	14.785745	0.009381	11.763313
115.000000	14.656627	0.009289	11.779719
116.000000	14.528670	0.009198	11.795980
117.000000	14.401863	0.009109	11.812103
118.000000	14.276193	0.009020	11.828094
119.000000	14.151649	0.008933	11.843959
120.000000	14.028219	0.008846	11.859703

Sorption trends
XEq = content sorbed at equilibrium sites in µg/g
XNeq = content sorbed at non-equilibrium sites in µg/g

Time (days)	Xeq (µg/g)	Xneq (µg/g)
0.000000	0.460871	0.000056
1.000000	0.447775	0.006597
2.000000	0.435249	0.012753
3.000000	0.423264	0.018544
4.000000	0.411796	0.023989
5.000000	0.400818	0.029104
6.000000	0.390307	0.033908
7.000000	0.380240	0.038416
8.000000	0.370596	0.042644
9.000000	0.361354	0.046606
10.000000	0.352495	0.050316
11.000000	0.343999	0.053788
12.000000	0.335851	0.057032
13.000000	0.328032	0.060062
14.000000	0.320527	0.062889
15.000000	0.313321	0.065523
16.000000	0.306400	0.067974
17.000000	0.299750	0.070252
18.000000	0.293358	0.072366
19.000000	0.287212	0.074325
20.000000	0.281299	0.076136
21.000000	0.275610	0.077809
22.000000	0.270133	0.079350
23.000000	0.264859	0.080765
24.000000	0.259777	0.082063
25.000000	0.254879	0.083249
26.000000	0.250156	0.084329
27.000000	0.245601	0.085310
28.000000	0.241204	0.086195
29.000000	0.236959	0.086991
30.000000	0.232859	0.087703
31.000000	0.228897	0.088334
32.000000	0.225067	0.088891
33.000000	0.221363	0.089375
34.000000	0.217778	0.089793
35.000000	0.214308	0.090147
36.000000	0.210948	0.090440
37.000000	0.207691	0.090677
38.000000	0.204535	0.090861
39.000000	0.201474	0.090994
40.000000	0.198503	0.091080
41.000000	0.195620	0.091121
42.000000	0.192820	0.091120
43.000000	0.190099	0.091080
44.000000	0.187454	0.091001
45.000000	0.184882	0.090888
46.000000	0.182380	0.090742
47.000000	0.179944	0.090565
48.000000	0.177572	0.090359
49.000000	0.175262	0.090125
50.000000	0.173009	0.089866
51.000000	0.170813	0.089583
52.000000	0.168670	0.089277
53.000000	0.166579	0.088951
54.000000	0.164538	0.088605

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 55.000000       0.162544       0.088240
 56.000000       0.160595       0.087858
 57.000000       0.158690       0.087461
 58.000000       0.156828       0.087048
 59.000000       0.155005       0.086622
 60.000000       0.153221       0.086183
 61.000000       0.151475       0.085733
 62.000000       0.149764       0.085271
 63.000000       0.148088       0.084799
 64.000000       0.146446       0.084318
 65.000000       0.144835       0.083828
 66.000000       0.143255       0.083331
 67.000000       0.141704       0.082826
 68.000000       0.140183       0.082315
 69.000000       0.138689       0.081798
 70.000000       0.137222       0.081276
 71.000000       0.135780       0.080749
 72.000000       0.134364       0.080218
 73.000000       0.132971       0.079682
 74.000000       0.131602       0.079144
 75.000000       0.130255       0.078603
 76.000000       0.128930       0.078059
 77.000000       0.127626       0.077513
 78.000000       0.126342       0.076965
 79.000000       0.125079       0.076416
 80.000000       0.123834       0.075866
 81.000000       0.122608       0.075315
 82.000000       0.121400       0.074763
 83.000000       0.120210       0.074211
 84.000000       0.119036       0.073660
 85.000000       0.117879       0.073108
 86.000000       0.116738       0.072557
 87.000000       0.115613       0.072007
 88.000000       0.114503       0.071458
 89.000000       0.113408       0.070910
 90.000000       0.112327       0.070363
 91.000000       0.111260       0.069817
 92.000000       0.110207       0.069273
 93.000000       0.109168       0.068731
 94.000000       0.108141       0.068191
 95.000000       0.107127       0.067652
 96.000000       0.106126       0.067116
 97.000000       0.105136       0.066582
 98.000000       0.104159       0.066051
 99.000000       0.103193       0.065521
100.000000       0.102238       0.064995
101.000000       0.101295       0.064471
102.000000       0.100362       0.063949
103.000000       0.099440       0.063430
104.000000       0.098529       0.062915
105.000000       0.097627       0.062402
106.000000       0.096736       0.061891
107.000000       0.095854       0.061384
108.000000       0.094982       0.060880
109.000000       0.094120       0.060379
110.000000       0.093266       0.059881
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111.000000	0.092422	0.059387
112.000000	0.091587	0.058895
113.000000	0.090761	0.058407
114.000000	0.089943	0.057921
115.000000	0.089133	0.057439
116.000000	0.088333	0.056961
117.000000	0.087540	0.056485
118.000000	0.086755	0.056013
119.000000	0.085978	0.055545
120.000000	0.085209	0.055079

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 objective function is based on observed mass of substance in soil and observed concentration of substance in liquid phase. The apparent sorption coefficient is calculated for each measurement. However, it is not used in optimization.
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
Kd	sorption coefficient (mL/g); ratio between total adsorbed concentration (µg/g) and the concentration in soil solution (µg/mL)
Kdapp	apparent sorption coefficient (mL/g); ratio between total adsorbed concentration (µg/g) and the concentration in soil solution (µg/mL)
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