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Evaluation of SorpKinAnalysis
Version 1.0 (27.08.2019)

By Mike Fuchs

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1. Abstract

In this report the software SorpKinAnalysis was evaluated against the already proven PEARLNEQ 5.1. Therefore, a dataset containing 131 chemical-soil combinations provided by the ECPA was parametrised with both tools. The resulting parameters of both tools were then compared against each other. And observed differences were analysed based on the data quality requirements of the guidance (CRD, 2016).

It was found that both tools can distinguish between acceptable and inacceptable datasets. For those fulfilling the requirements stated in the guidance (CRD, 2016), SorpKinAnalysis 1.0 agrees well with PEARLNEQ 5.1 concerning the optimised parameters. For SorpKinAnalysis to fulfil all requirements stated in the EFSA scientific opinion some minor changes need to be done.

2. Introduction

The adsorption of chemicals to soil is highly important for their transport behaviour and therefore effects the potential of the chemical to move to groundwater or surface water. Equilibrium sorption describes sorption to be instantaneous and fully reversible hence, sorption does not change over time. Non-equilibrium (aged/kinetic) sorption on the other hand describes the sorption to increase over time. Kinetic sorption has a significant effect on the leaching behaviour of chemicals and was therefore implemented into the regulatory risk assessment for pesticides (Hardy, 2011; Van Beinum & Beulke, 2012).

The draft guidance (Van Beinum & Beulke, 2012 and CRD, 2016) propose the tool PEARLNEQ 5.1 to be suitable to estimate the parameters needed for the two-site one-rate kinetic sorption model. Since this tool is based on text files for input and batch files to run the tool and does not have a graphical user interface (GUI) it may not be easy to apply for unexperienced users. Therefore, EFSA require the development of a user-friendly tool in their scientific opinion about the aged sorption guidance (EFSA, 2018).

The software package SorpKinAnalysis 1.0 was developed as a user-friendly implementation of the two-site one-rate kinetic sorption model (Klein & Klein, 2019). SorpKinAnalysis 1.0 uses a graphical user interface, provides a graphical representation of the fit and substantial statics for the goodness of fit. The main difference to PEARLNEQ 5.1 is the solver used for the non-linear optimization. While PEARLNEQ 5.1 relies on PEST which uses the Gauss-Marquardt-Levenberg method (Doherty, 2015), SorpKinAnalysis 1.0 uses the NelderMeadSolver Class by Microsoft Solver Foundation.

Experimental aged sorption studies according to the design described in the guidance (CRD, 2016) were provided by the European Crop Protection Association (ECPA) and used to test the draft guidance versus experimental data sets (Hardy, 2011).

The work presented in this report is based on the same data sets to evaluate SorpKinAnalysis 1.0 versus the most recent version of PEARLNEQ (version 5.1). It should be tested whether the parameters estimated with SorpKinAnalysis 1.0 agree with the parameters estimated with PEARLNEQ 5.1.

3. Material and Methods

3.1. Study data

The dataset used in this evaluation was provided by the European Crop Protection Association (ECPA). A preselection was made based on the data quality check by Hardy (2011). A total number 28 studies have been selected. Some of them did not meet all requirements of the draft guidance but were declared as “acceptable for further evaluation in spite of some deficiencies” (Hardy, 2011). The 28 studies comprised of 131 soil-chemical combinations, which all were analysed individually. For the parametrization some outliers were removed from the data, but measurements on Day-0 and Day-1 were included if available according to the recommendation of the most recent version of the guidance (CRD, 2016; EFSA, 2018). The following five parameters were optimised:

- initial mass of pesticide [µg],
- equilibrium $K_{f,oc}$ [L/kg],
- f_{NE} (ratio between equilibrium and non-equilibrium Freundlich coefficients [-],
- k_{des} (desorption rate constant) [1/d],
- $DegT_{50eq}$ *(first order* transformation half-life in equilibrium sorption phase) [d].

3.2. PEARLNEQ

PEARLNEQ 5.1 consists of the optimisation software PEST and the two-site one-rate model which is implemented in FOCUS PEARL. PEARLNEQ 5.1 fits the estimated total mass of pesticide in soil [µg] and the concentration in the liquid phase [µg/L] versus the corresponding measured values at different time points. The Gauss-Marquardt-Levenberg algorithm and the least squares method are used to adjust the parameters until the best fit to the experimental data is archived. For this evaluation PEARLNEQ 5.1 which is the most recent version was used.

The program uses a text input file with the ending *.mkn (Appendix 1) and a batch file to call the programs pearlmk, pestcheck, tempcheck, inscheck and pest. To avoid local minima of the optimisation-function the draft guidance (CRD 2016) demands to test at least four different initial guesses for f_{NE} and k_{des} (Table 1). Four combinations per soil-chemical combination resulted in 604 PEARLNEQ 5.1 runs. They were executed in an automated workflow. The *.mkn-files were generated using R-scripts and the batch-files called by a parent batch-file.

Table 1: Initial guesses for f_{NE} and k_{des}.

f_{NE}	k_{des}
0.2	0.004
0.2	0.05
1.5	0.004
1.5	0.05

PEARLNEQ 5.1 produces a lot of files which are needed for the optimisation. The record-file contains the different parameter combinations used during optimisation, the final parameter values with upper and lower 95% confidence limits, the observed vs calculated values for each timepoint, the correlation matrix for the parameters. The output-file contains the final parameters, a table with the predictions in timesteps of 1 hour of: mass of pesticide, concentrations in liquid phase, equilibrium sorbed phase, non-equilibrium sorbed phase and apparent K_d which is the quotient of the total adsorbed phase concentration (equilibrium and non-equilibrium) and the liquid phase concentration. PEARLNEQ 5.1 does not provide the Chi²-error of the fit and relative standard error (RSE) for each parameter which must be calculated externally.

3.3. SorpKinAnalysis

The software SorpKinAnalysis 1.0 was developed at the Fraunhofer Institute for Molecular Biology and Applied Ecology (IME) and was used for the present evaluation. SorpKinAnalysis 1.0 uses a graphical user interface with two input windows. In the first windows “Experimental Data” the experimental data can be entered manually or inserted via copy-paste into a table (Appendix 2). In the second window “Parameters” the parameter values, their initial guesses and a selection of those parameter which should be estimated need to be entered (Appendix 3). Furthermore, the upper and lower limit of each parameter must be set (see Appendix 3 for default limits). For the current exercise default limits were used with the exception that the lower limit of the DT50_EQ was changed from 0 to 0.1 to avoid a crash of the program during optimisation. Under the tag “Program” and “settings” the objective function can be selected. For the present work the default setting “Weighted least squares Value” was used. It means that the values were weighted according to their individual value which corresponds to the setting of PEARLNEQ 5.1.

SorpKinAnalysis 1.0 outputs one report text-file and 6 plots. The report contains the users input of experimental data and parameters, the result of parameter fitting, a detailed statistical evaluation of the fit, observed vs calculated values for each timepoint and the prediction for mass of pesticide and concentration in liquid phase by time steps of one day. The apparent K_d and the RSE of the parameters are not provided by the software. Three plots each belong to the mass of pesticide in soil and concentration in liquid phase. One plot shows the experimental data as points and the model prediction as a curve against time. Another plot shows the experimental data against the predicted values with a 1:1 line of identity and the last plot shows the residuals between experimental data and model prediction against the time.

As with the optimisation with PEARLNEQ 5.1 four combinations of initial guesses of the parameters f_{NE} and k_{des} (Table 1) were used to avoid local minima of the optimisation-function. The resulting 604 SorpKinAnalysis runs were performed manually since an automated workflow was not possible.

3.4. Mathematical background

The mathematical background of the two-site one-rate model is explained in detail in the documentations of SorpKinAnalysis 1.0 (Klein J. & Klein M., 2019) and PEARLNEQ 5.1 (Boesten & ter Horst, 2012).

For the present evaluation the *Chi²*-error was calculated as following (Van Beinum & Beulke, 2012):

$$Chi^2 = 100 * \sqrt{\frac{1}{X^2_{tab}} * \sum_{i=1}^{N} \frac{(P_i - O_i)^2}{{O_i}^2}} \qquad 1$$

where X^2_{tab} is the standard tabulated value at the 5% significance level and the given degrees of freedom, P_i is the predicted value of the measurement i and O_i is the observed value of the measurement i (replicates must be averaged). The relative standard error (RSE) of the parameters was calculated as documented in Van Beinum & Beulke (2012):

$$RSE = \frac{u_l - l_l}{4 * V_i} \qquad 2$$

where u_l is the 95% confidence interval upper limit, l_l is the 95% confidence interval lower limit and V_i is the fitted value of the parameter i. The relative differences between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 were calculated as following:

$$relativ\ difference = 100 * \frac{V_{S,i} - V_{P,i}}{V_{P,i}} \quad 3$$

where $V_{S,i}$ is the value of the parameter i fitted by SorpKinAnalysis 1.0 and $V_{P,i}$ is the value of the parameter i fitted by PEARLNEQ 5.1.

4. Results

4.1. Complete dataset

As described earlier for each soil-chemical combination four optimisation runs were performed. To compare both tools one set of parameters for each soil-chemical combination was selected. Therefore, the runs with the best goodness-of-fit based on the Chi²-error were chosen. Find fitted and averaged parameters in Appendix 4 and 5.

As a visual representation of the match between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 the estimated parameters are plotted against each other. For better detail of the differences between both tools and to identify perhaps existing trend the relative difference (Formula 3) are plotted against the estimated values by PEARLNEQ 5.1 as well.

For the initial mass of pesticide both tools agree very well (Figure 1). The relative difference shows that only 3 out of 131 datapoint differ more than 5 percent (Figure 2).

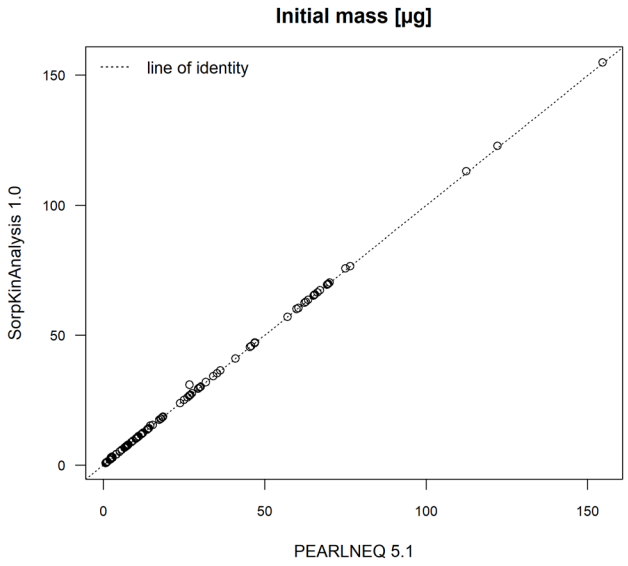

Figure 1: Initial mass of pesticide [µg] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1, for the complete dataset.

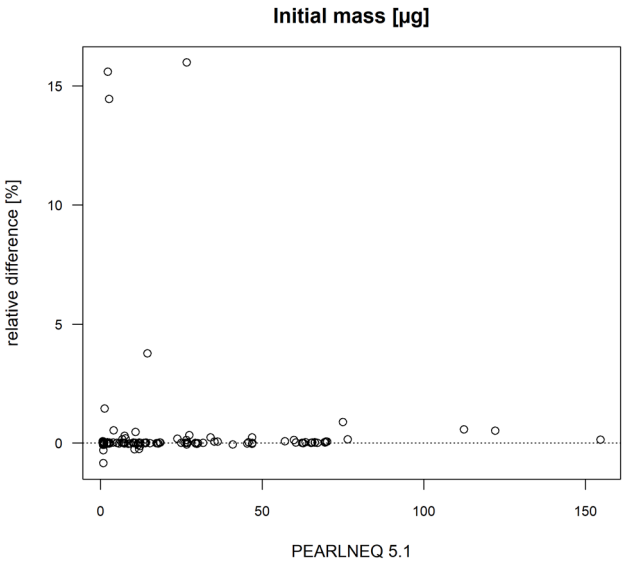

Figure 2: Relative difference of the initial mass of pesticide between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the complete dataset.

The estimated equilibrium $K_{f,oc}$ of SorpKinAnalysis 1.0 agrees well with the estimates of PEARLNEQ 5.1 (Figure 3). However, several data points differ significantly.

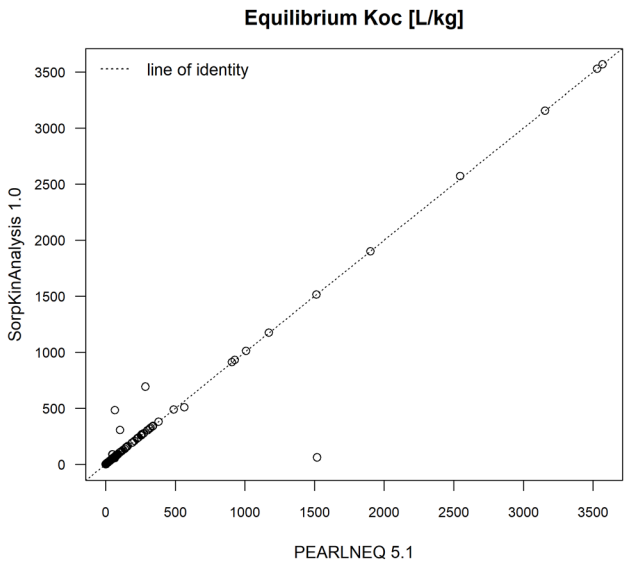

Figure 3: Equilibrium Koc [L/kg] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the complete dataset.

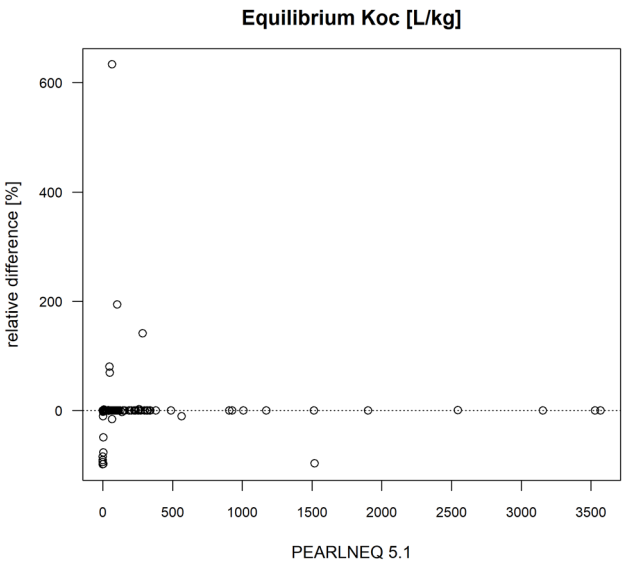

Figure 4: Relative difference of the equilibrium Koc between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the complete dataset.

The estimated f_{NE}-value which is the ratio between equilibrium and non-equilibrium Freundlich coefficients is the parameter with the highest number of deviations between both tools (Figure 5). Up to a value of 2 the data points are on the line of identity. For higher values the estimations of the tools mostly differ significantly. Which is also reflected in the differences plot (Figure 6). There are a few datapoints with a value of 10 on the X-axis in Figure 5. Which is explained by the upper limit of 10 for this parameter set in PEARLNEQ 5.1, versus a default upper limit of 10000 in SorpKinAnalysis 1.0. The guidance states that the value of the parameter needs to be below 10.

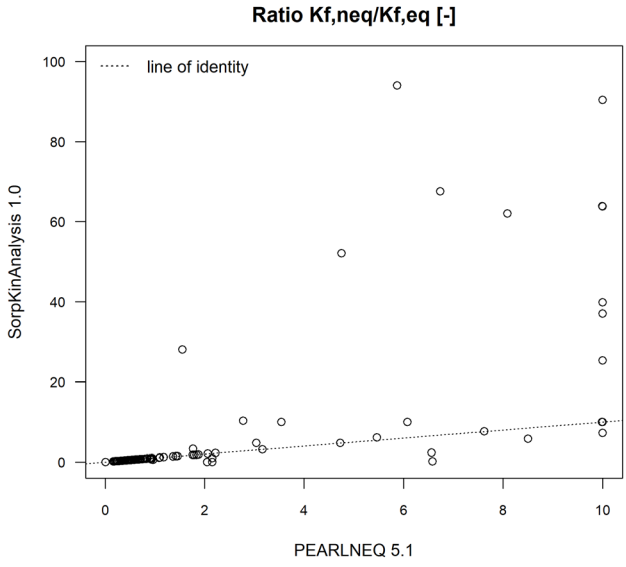

Figure 5: Ratio between equilibrium and non-equilibrium Freundlich coefficients [-] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the complete dataset.

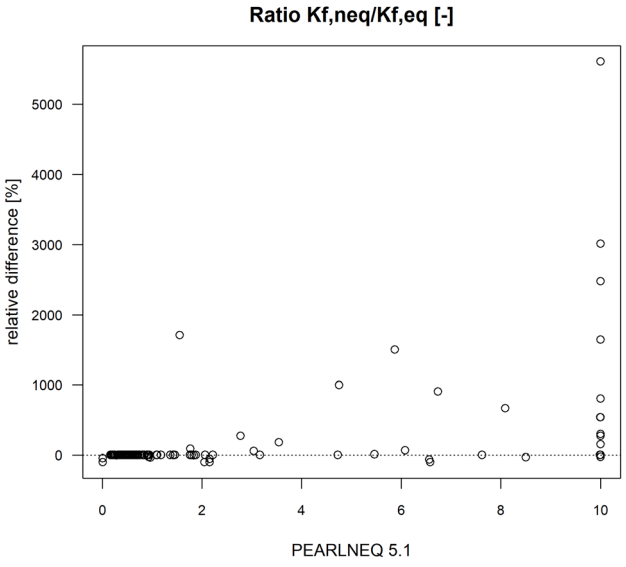

Figure 6: Relative difference of the ratio between equilibrium and non-equilibrium Freundlich coefficients between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the complete dataset.

The estimates of the desorption rate constant k_{des} agrees well for most of the data sets (Figure 7). The relative differences show some scattering around the zero-deviation line, mainly between 0 and 0.5% (Figure 8). It needs to be mentioned that the current version of SorpKinAnalysis 1.0 only reports three decimals for the desorption rate constant leading to only two significant decimals in some cases. The datapoints at -100% represent cases for which the estimated desorption rate constant of SorpKinAnalysis is 0 and the value for PEARLNEQ 5.1 is in the order of 10^{-5}. It is not clear if SorpKinAnalysis 1.0 estimates a value of 0 or if this is a rounding error.

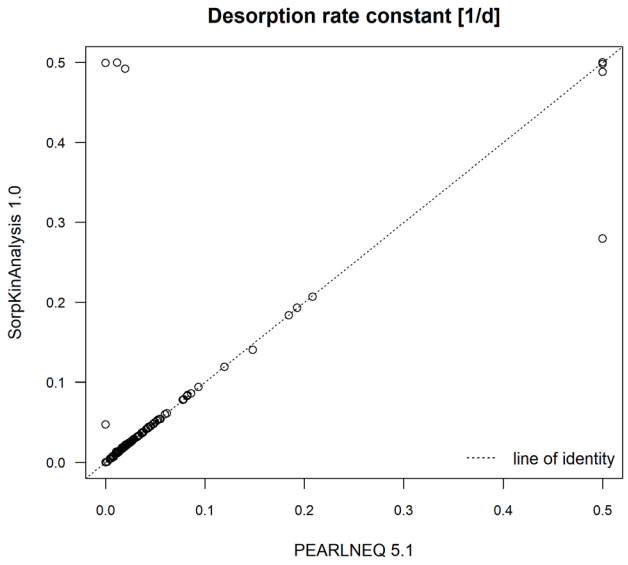

Figure 7: Desorption rate constant [1/d] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the complete dataset.

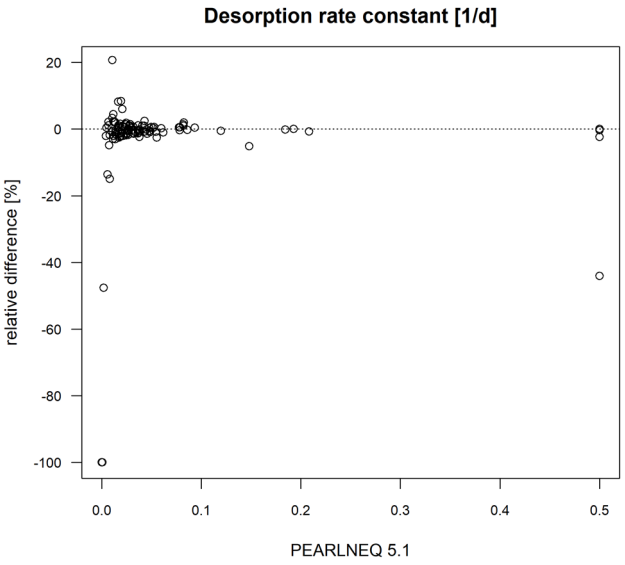

Figure 8: Relative difference of the desorption rate constant between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the complete dataset.

The estimations of the transformation half-life DegT50eq of the different tools agree well (Figure 9). There is a small number of less than 10 values for which the tools deviate from each other.

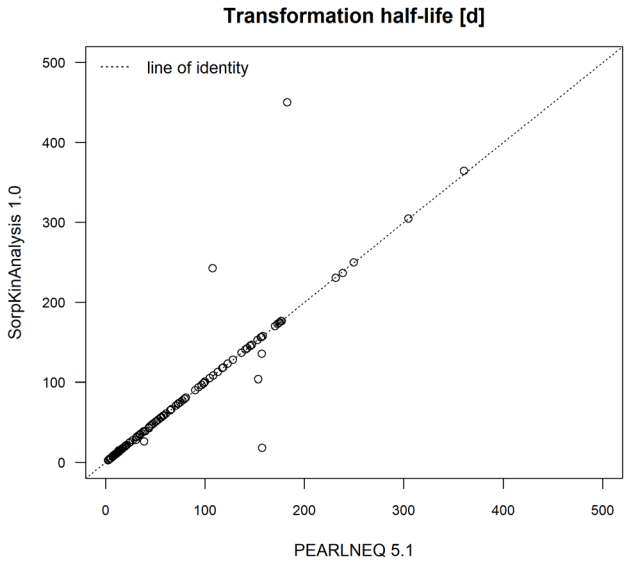

Figure 9: Transformation half-life [d] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the complete dataset.

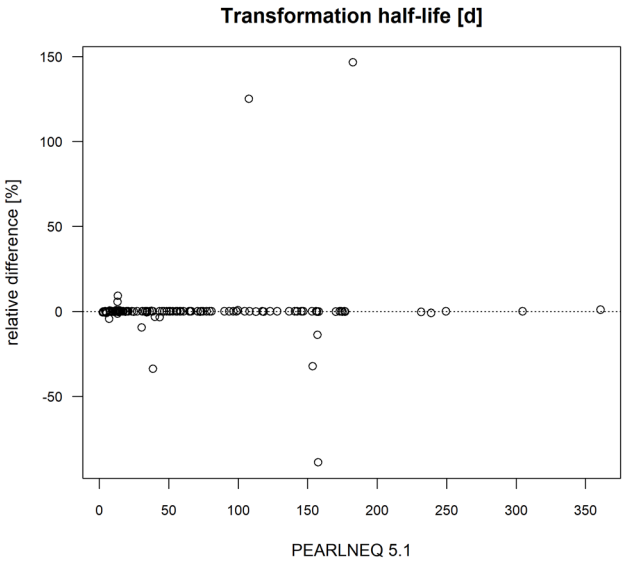

Figure 10: Relative difference of the transformation half-life between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the complete dataset.

4.2. Analysis of deviations and exclusion of data sets from the comparison

Due to the deviations regarding the comparison between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 some analysis of the reasons was carried out. In a first step all datasets with a deviation of higher than 5 percent for one of the parameters were chosen. These datasets were then checked versus the quality criteria of the guidance. It could be shown that these for clear reasons do not fulfil the quality criteria of the guidance. Hence, were excluded from the comparison since the estimated parameters do not represent meaningful estimates of the aged sorption process. In Table 2 an overview of the data sets and a detailed description of the reasons of exclusion are shown.

Table 2: Excluded studies with the reasons for the exclusion.

ID	bad visual fit	Chi² > 15 %	RSE > 0.4 of one or more parameters	first day after day 3	Chi²-error SorpKinAnalysis 1.0	Chi²-error PEARLNEQ 5.1
ECPA-02A	X		X		6.282	6.897
ECPA-02B	X	X	X		26.780	26.769
ECPA-02D	X		X		9.106	9.971
ECPA-02E	X		X		7.006	7.010
ECPA-05D			X		2.279	2.411
ECPA-13D	X		X		7.023	7.063
ECPA-23A	X		X		8.120	8.910
ECPA-24A			X	X	2.895	3.180
ECPA-24B			X	X	7.259	7.675
ECPA-24C	X		X	X	13.494	14.837
ECPA-24D			X	X	4.956	5.439
ECPA-27A			X		4.829	5.452
ECPA-27B			X		12.434	32.890
ECPA-27C		X	X		15.461	16.954
ECPA-27D			X		14.546	35.449
ECPA-28C			X	X	10.225	10.751

ECPA-28G	X		X	X	14.606	5.365
ECPA-28I	X			X	14.792	3.071
ECPA-28L			X	X	4.189	4.660
ECPA-30A		X	X		25.067	26.716
ECPA-30C	X		X		8.578	9.408
ECPA-32B			X	X	8.600	9.700
ECPA-35A	X				14.419	12.690
ECPA-35C		X	X		27.467	23.970
ECPA-35D		X	X		24.974	22.179
ECPA-38A	X		X		12.607	12.642
ECPA-38B	X		X		11.692	11.695
ECPA-38C	X	X	X		25.169	25.176
ECPA-38F			X		5.915	5.918
ECPA-38G			X		10.721	10.818
ECPA-38J	X		X		10.618	10.623
ECPA-38P			X		13.791	13.821
ECPA-41B			X	X	6.575	6.551
ECPA-43A			X	X	8.892	8.551
ECPA-43B			X	X	11.059	11.057
ECPA-43C			X	X	11.554	11.557
ECPA-43D		X	X	X	20.519	20.522
ECPA-44B			X	X	2.501	2.591

4.3. Subset

In the following the comparison of SorpKinAnalysis 1.0 and PEARLNEQ 5.1 for the subset is presented. The relative difference of the initial mass and transformation half-life are negligible (mostly below 0.5%, see Figures 12 and 14).

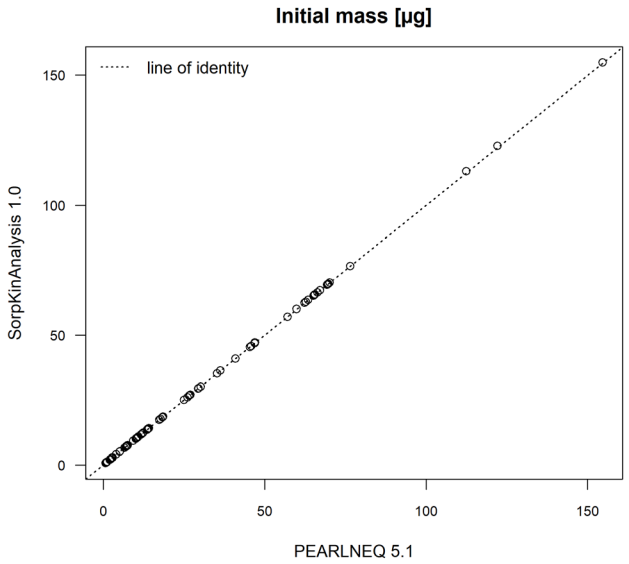

Figure 11: Initial mass of pesticide [µg] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the subset.

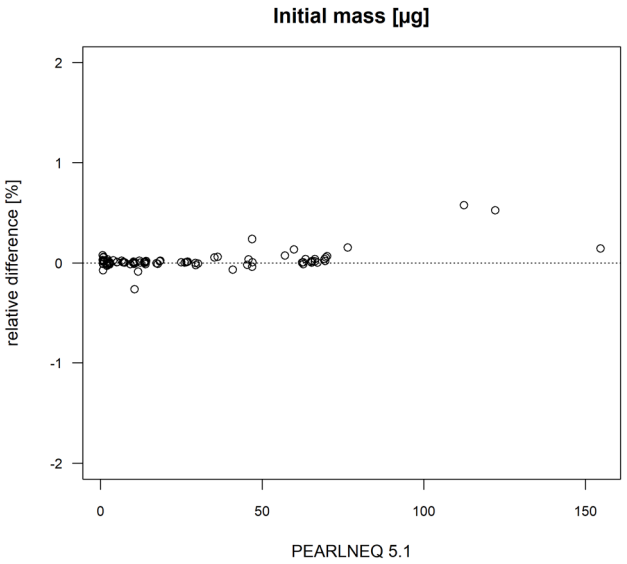

Figure 12: Relative difference of the initial mass of pesticide between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the subset.

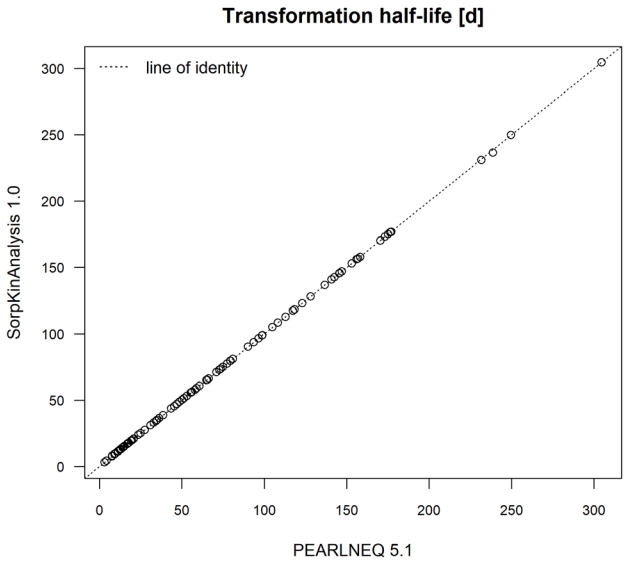

Figure 13: Transformation half-life [d] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the subset.

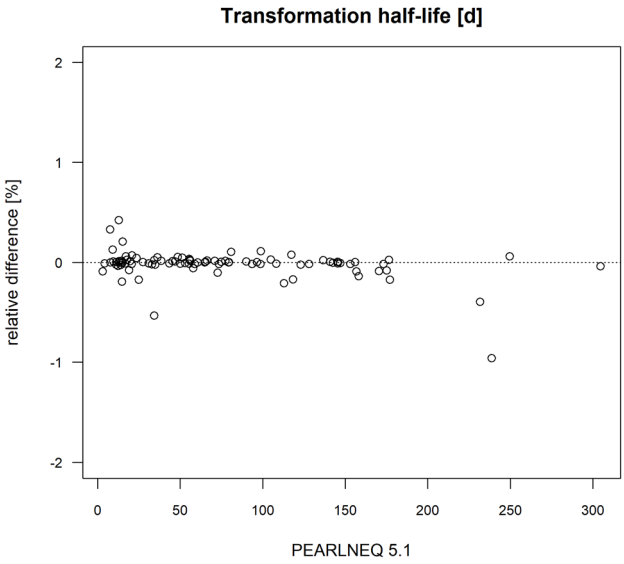

Figure 14: Relative difference of the transformation half-life between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the subset.

For the equilibrium $K_{f,oc}$ SorpKinAnalysis 1.0 and PEARLNEQ 5.1 match very well. The relative differences are below one percent (Figure 16). Same holds true for the ratio between equilibrium and non-equilibrium Freundlich coefficients (f_{NE}).

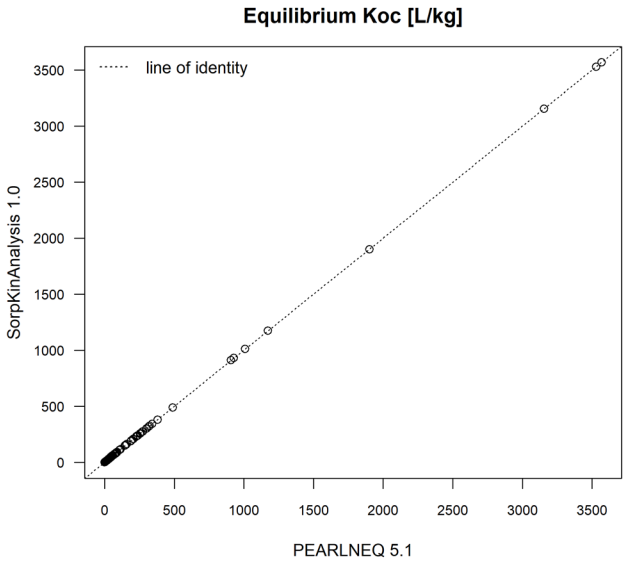

Figure 15: Equilibrium Koc [L/kg] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the subset.

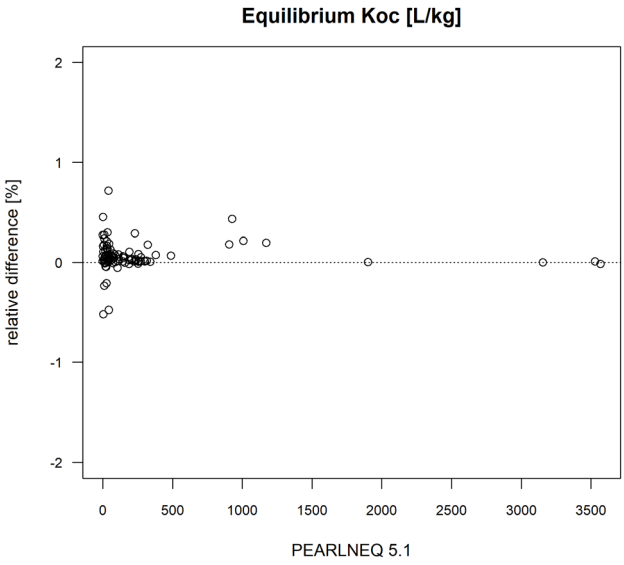

Figure 16: Relative difference of the equilibrium Koc between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the subset.

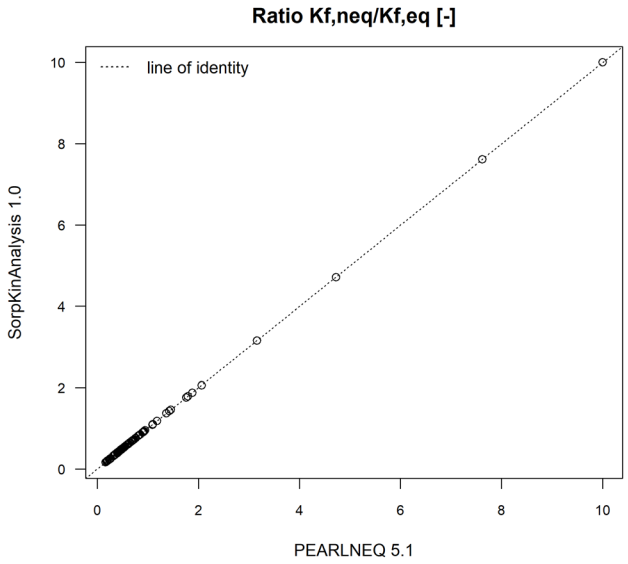

Figure 17: Ratio between equilibrium and non-equilibrium Freundlich coefficients [-] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the subset.

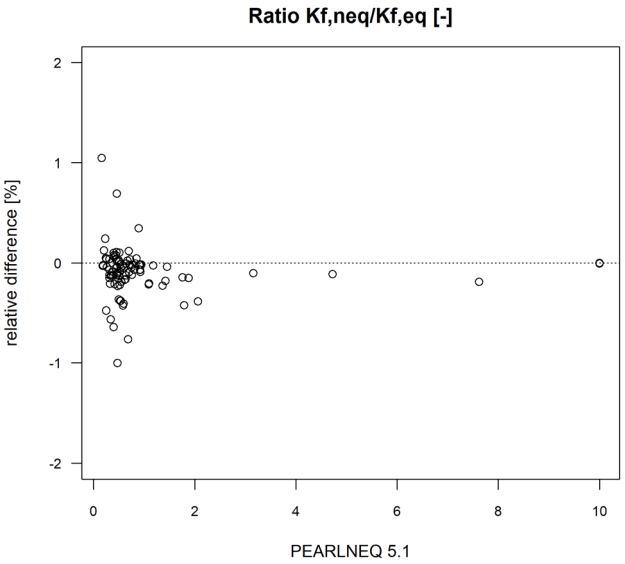

Figure 18: Relative difference of the ratio between equilibrium and non-equilibrium Freundlich coefficients between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the subset.

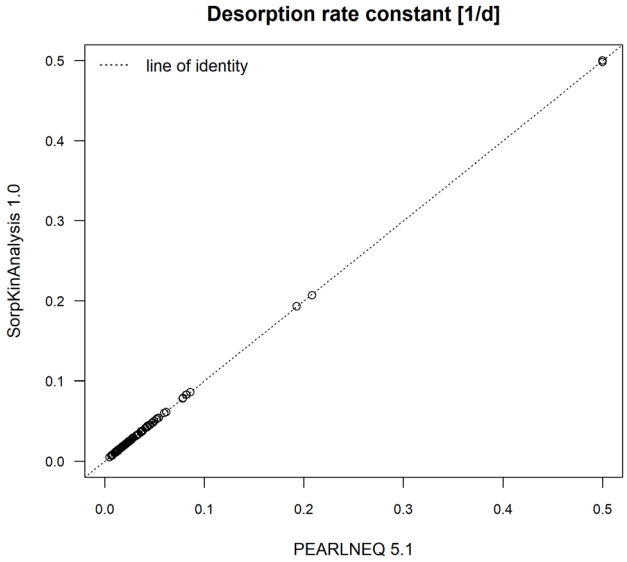

Figure 19: Desorption rate constant [1/d] for SorpKinAnalysis 1.0 against PEARLNEQ 5.1 for the subset.

The relative difference of the desorption rate constant is the highest amongst the five parameters (Figure 21). As already described earlier SorpKinAnalysis reports only three decimal numbers for the desorption rate constant. Figure 20 shows the same data as Figure 21 but the results of PEARLNEQ 5.1 have been rounded to 3 decimals too. This suggests that both tools calculate very similar values for the desorption rate constant internally and only differ in reporting.

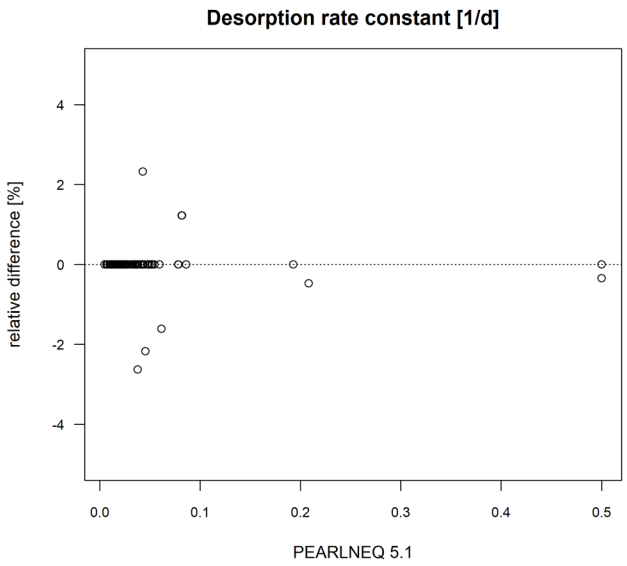

Figure 20: Relative difference of the desorption rate constant between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the subset, based on to three decimals rounded values of PEARLNEQ.

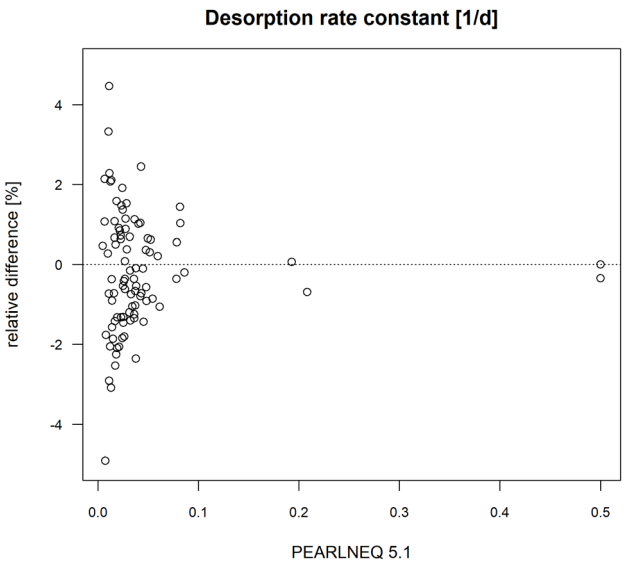

Figure 21: Relative difference of the desorption rate constant between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 against the fitted value by PEARLNEQ 5.1, for the subset.

5. Discussion

The results of the complete dataset show a considerable probability that experimental data of insufficient quality concerning the criteria defined in the guidance (CRD, 2016) result in a local minimum of the optimisation function and show significant differences of the estimated parameters between tools with a different solver. Therefore, a subset of data fulfilling the quality criteria was used.

The subset showed that the differences between SorpKinAnalysis 1.0 and PEARLNEQ 5.1 are neglectable. The biggest discrepancy between both tools was found for the estimated desorption rate constant. It was found that this could be explained by rounding effects since SorpKinAnalysis 1.0 only reports three decimal digits while PEARLNEQ 5.1 reports 6 digits.

In addition, a problem was identified that caused SorpKinAnalysis to crash. In these cases the solver set the transformation half-life to 0 days. The problem was fixed by setting the lower limit of "DT50_EQ" to 0.1 days.

The draft guidance (CRD, 2016) recommends an upper limit of 10 for the ratio between equilibrium and non-equilibrium Freundlich coefficients (f_{NE}) to avoid convergence at unrealistic local minima. Changing the default setting in SorpKinAnalysis 1.0 from 10000 to 10 would not only insure compliance with the guidance but would also improve the performance of the fitting procedure.

At the tested state of the software all information on the apparent K_d were missing in the results of SorpKinAnalysis. Since the visual fit of the apparent K_d is required by the draft guidance (CRD, 2016) it would be desirable that SorpKinAnalysis 1.0 provides these plots. Furthermore, a graphical representation of the sorption trends (equilibrium sorption vs non-equilibrium sorption) would be helpful.

The EFSA scientific opinion lists the use of a graphical user interface as a requirement to facilitate the use by regulators (EFSA, 2018). This is fulfilled by SorpKinAnalysis 1.0 and the tool is easy to understand and to apply for users. But, more than 600 optimisation runs have shown a major shortcoming. While optimisation using PEARLNEQ 5.1 can be executed using a batch-file optimisation with SorpKinAnalysis 1.0 took much longer time since each run had to be executed manually. To simplify optimisation of a large number of data sets and to enable automated workflows a possibility for automated data procession would be helpful. This is also listed as a requirement by EFSA (2018).

SorpKinAnalysis 1.0 is not providing the relative standard errors (RSE) nor the 95% confidence intervals of the fitted parameters. Since the guidance require an RSE below 0.4 this information must be given.

6. Conclusion

Both tools can distinguish between acceptable and inacceptable datasets. For those fulfilling the requirements stated in the guidance (CRD, 2016), SorpKinAnalysis 1.0 agrees well with PEARLNEQ 5.1 concerning the optimised parameters. The graphical user interface is very user friendly and if a small number of optimisations should be done. Furthermore, SorpKinAnalysis provides a detailed statistical evaluation and a graphical representation of the fit.

To meet all requirements the following changes need to be implemented:

- add apparent K_d values and corresponding plots
- add relative standard error (RSE)
- change the default lower limit of transformation half-life
- change the default upper limit of f_{NE}
- report at least three significant decimals on f_{NE} and k_{des}
- add possibility for automated data procession

7. References

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

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Hardy I., 2011. Evaluation of aged-sorption studies: Testing of the draft guidance. Battelle report number PS/10/001A.

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Van Beinum W. and Beulke S., 2012. Consideration of additional experimental data sets to support the development of the revised guidance on aged sorption studies. The Food and Environment Research Agency, York.

Doherty, J., 2015. Calibration and uncertainty analysis for complex environmental models. Watermark Numerical Computing, Brisbane, Australia. 227pp. ISBN: 978-0-9943786-0-6 Downloadable from www.pesthomepage.org.

Boesten, J.J.T.I. and ter Horst, M.M.S., 2012. Manual of PEARLNEQ v5

8. Appendix

Appendix 1: Example input-file for PEARLNEQ 5.1 (ECPA-01A)

```
*-------------------------------------------------------------------------------
----------
* STANDARD FILE for pearlmk version 5
* Program to fit the half-life, activation energy and parameters for long-term
sorption
* kinetics of pesticides in soil
*
* This file is intented for use with the PEST program (Doherty et al., 1991).
* Please refer to the manual of PEARLNEQ
*
* (c) Alterra 2012
*-------------------------------------------------------------------------------
----------

* Model control
Yes              ScreenOutput
0              TimStart          (d)              Start time of experiment
120            TimEnd            (d)              End time of experiment
0.01            DelTim           (d)            Time step of Euler's integration
procedure

* System characterization
8.042            MasIni            (ug)            Initial guess of initial mass
100            MasSol            (g)             Mass of soil in incubation jar
27.7             VolLiqSol         (mL)            Volume of liquid in the moist
soil
72.3              VolLiqAdd         (mL)             Volume of liquid ADDED
0.043            CntOm             (kg.kg-1)       Organic matter content

* Sorption parameter
1              ConLiqRef         (mg.L-1)        Reference liquid concentration
0.91             ExpFre            (-)             Freundlich exponent
5.8584686774942              KomEql            (L.kg-1)         Initial guess of
Coefficient for equilibrium sorption
0.2                FacSorNeqEql       (-)               Initial guess of ratio
KfNeq/KfEql
0.004             CofRatDes         (d-1)            Initial guess of desorption
rate constant
Neql              OptSor            (-)              Option for type of sorption
process to be simulated: 'Neql' or 'Eql'

* Transformation parameters
90             DT50Ref           (d)              Initial guess of half-life at
ref. temperature
20.0             TemRefTra         (C)              Reference temperature
65.4           MolEntTra        (kJ.mol-1)      Initial guess of molar activation
energy

* Temperature at which the incubation experiments have been carried out
table Tem (C)
1  20
end_table

* Number of replicate sets (range 1 - 9)
```

```
* A set of replicates can contain observation at different time points and
temperatures
* Each replicate set should contain at least one measurement performed at each of
the temperatures specified in table Tem
* 1st sort by Rep. (column 5), 2nd sort by Tem (column 2), 3rd sort by Tim (column
1)
* specify missing values or values you do not want to include in the optimisation
procedure (e.g. outliers) as -99.999
*  PEARLMK will give these observations a weight of zero, meaning that the
observation takes to part in the optimisation
2                NumRepSet          (-)

* Provide the results of the measurements
* Tim  Tem  Mas       ConLiq    Rep.  observation ID
* (d)  (C)  (ug)      (ug/mL)
table Observations
0     20    7.62147008859768  0.0577913224274406      1     OBS
1     20    7.73493384229136  0.0560552538258575      1     OBS
3     20    7.3183890345125   0.0526787155672823      1     OBS
7     20    6.9381307846003   0.0483311377308707      1     OBS
14    20    6.43574368932528  0.0437978089709763      1     OBS
30    20    5.57502013901345  0.0354252432717678      1     OBS
58    20    4.55611077589107  0.0275040981530343      1     OBS
120   20    3.36078919564302  0.018991619525066 1     OBS
0     20    7.61522008198517  0.056794546701847 2     OBS
1     20    7.64106021008898  0.0559363852242744      2     OBS
3     20    7.35278970221662  0.0517144274406332      2     OBS
7     20    7.09329274261159  0.0485153535620053      2     OBS
14    20    6.40314992666776  0.0434929393139842      2     OBS
30    20    5.52581992921649  0.0360773403693931      2     OBS
58    20    4.56964952326203  0.0270766649076517      2     OBS
120   20    3.30338179211549  0.0188166459102902      2     OBS
end_table

* Option for weights of Observations:
*'equal' gives equal weights to all measurements
*'inverse' gives weigth equal to inverse value of each measurement (if measurement
is zero then weight is 1.0)
inverse    Opt_weights

* Option for description of transformation rate
* 'EqlDom' uses rate based on amount of substance in equilibrium domain
* 'LiqPhs' uses rate based on amount of substance in liquid phase
EqlDom     Opt_transformation
```

Appendix 2: Experimental data page of SorpKinAnalysis 1.0 (ECPA-01A)

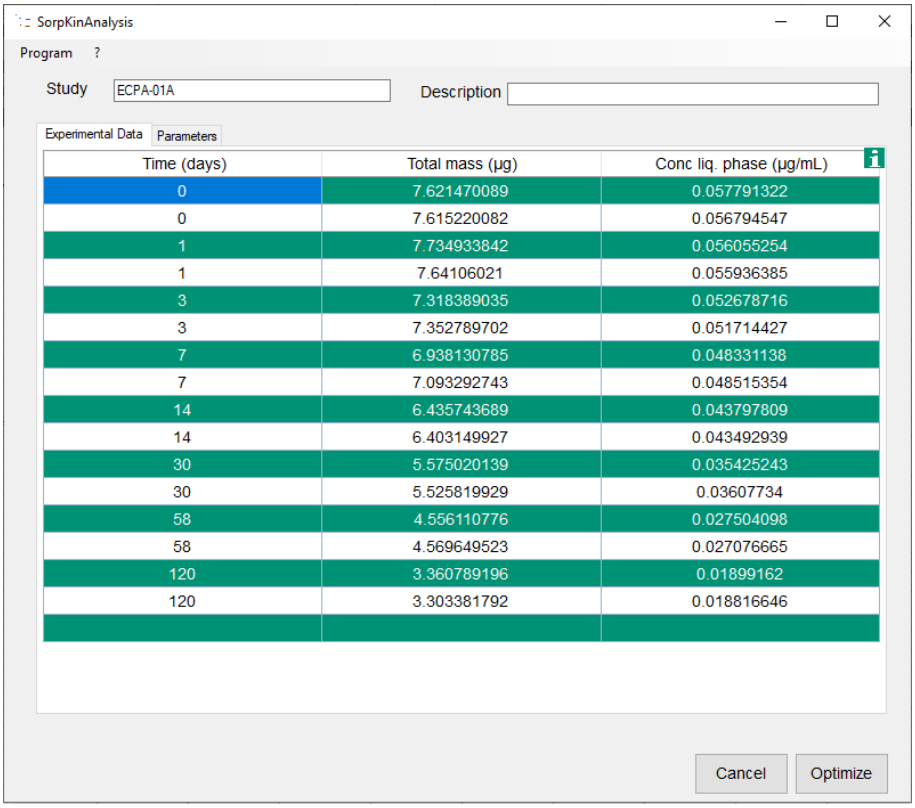

Figure A 1: Experimental data page of SorpKinAnalysis 1.0 (ECPA-01A)

Appendix 3: Parameter data page of SorpKinAnalysis 1.0 (ECPA-01A)

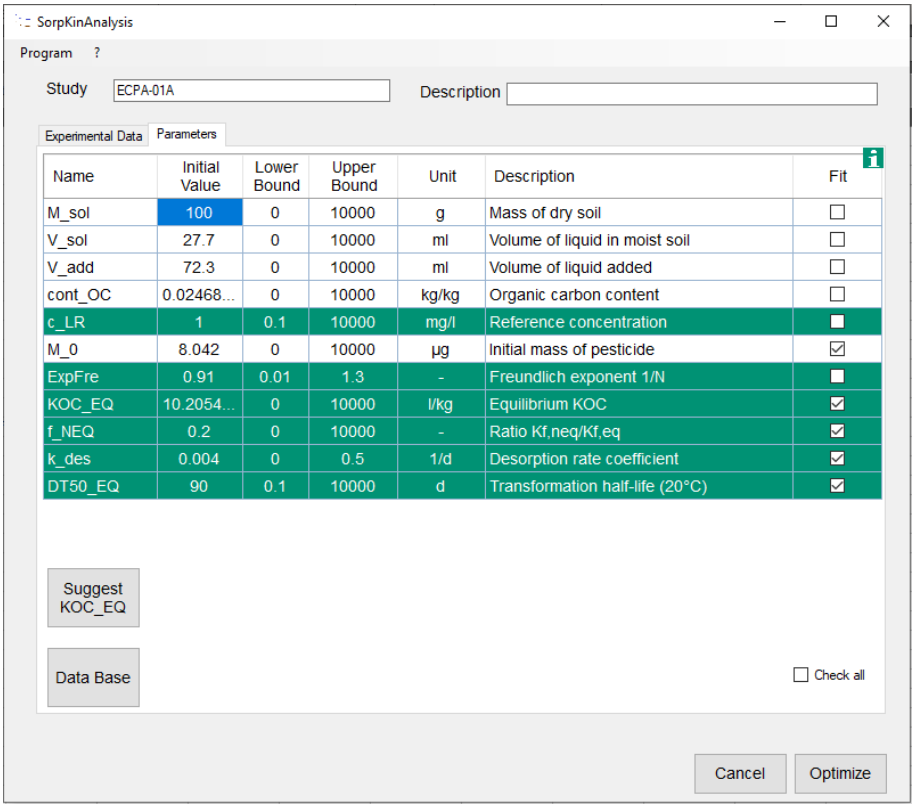

Figure A 2: Parameter data page of SorpKinAnalysis 1.0 (ECPA-01A)

Appendix 4: Fitted parameters of PEARLNEQ 5.1

Table A 1: Fitted parameters of PEARLNEQ 5.1.

ID	initial mass	equilibrium $K_{f,oc}$	f_{NE}	k_{des}	$DegT_{50eq}$	Chi²-error
ECPA-01A	7.343	9.090	0.583	0.050	79.490	2.823
ECPA-01B	6.901	12.652	0.463	0.078	93.620	4.982
ECPA-01C	7.512	8.366	0.440	0.043	60.660	1.914
ECPA-01D	7.192	9.414	0.515	0.048	142.580	2.165
ECPA-02A	31.796	14.124	9.990	0.000	12.090	6.897
ECPA-02B	33.992	11.809	6.078	0.000	4.990	26.769
ECPA-02C	36.268	56.631	0.186	0.037	4.290	Inf
ECPA-02D	29.821	13.009	3.548	0.000	10.270	9.971
ECPA-02E	26.630	4.992	10.000	0.000	21.170	7.010
ECPA-03A	18.515	60.224	0.704	0.017	30.960	4.628
ECPA-03B	17.711	41.405	0.401	0.060	46.890	3.853
ECPA-03C	17.340	114.595	0.905	0.019	14.550	10.007
ECPA-03D	18.287	48.646	0.361	0.036	53.050	2.724
ECPA-04A	10.255	34.989	0.437	0.048	145.770	1.051
ECPA-04B	10.202	32.234	0.183	0.086	128.100	1.945
ECPA-04C	10.270	41.706	0.476	0.053	145.410	1.005
ECPA-04D	10.226	45.466	0.317	0.045	173.170	1.225
ECPA-05A	7.313	2.432	0.525	0.013	140.830	0.893
ECPA-05B	7.000	0.442	2.066	0.016	156.100	1.673
ECPA-05C	7.381	3.714	0.343	0.012	64.940	1.197
ECPA-05D	7.397	1.118	10.000	0.000	117.450	2.411
ECPA-06A	67.156	341.719	0.715	0.041	108.290	1.553
ECPA-06B	62.298	302.560	0.612	0.027	90.070	2.070
ECPA-06C	66.273	380.078	0.614	0.052	177.120	2.428
ECPA-06D	65.330	316.311	0.672	0.034	77.410	1.007
ECPA-07A	45.377	74.221	0.753	0.033	55.650	3.469
ECPA-07B	47.038	81.244	0.314	0.037	45.400	2.317
ECPA-07C	46.903	106.538	0.698	0.037	80.970	2.467
ECPA-07D	45.755	69.381	0.474	0.028	50.160	1.908
ECPA-08A	12.023	151.756	0.390	0.022	98.700	6.321
ECPA-08B	12.295	113.289	0.495	0.017	104.840	5.335
ECPA-09A	2.818	3529.297	0.318	0.500	98.820	3.786
ECPA-09B	2.805	3155.072	0.193	0.500	79.500	1.877
ECPA-09C	2.725	3568.047	0.262	0.500	43.550	2.199
ECPA-09D	2.731	1901.519	0.244	0.500	55.450	2.315
ECPA-11A	69.470	206.691	0.540	0.025	156.820	2.136
ECPA-11B	69.678	255.999	0.551	0.025	158.100	2.781
ECPA-11C	69.316	273.017	0.474	0.023	238.840	3.259
ECPA-11D	70.118	192.908	0.585	0.021	112.930	3.750
ECPA-11E	65.117	192.930	0.524	0.021	153.100	3.946
ECPA-11F	62.765	188.569	0.491	0.037	304.640	1.545
ECPA-11G	66.353	227.070	0.470	0.038	170.430	2.012
ECPA-11H	63.464	160.390	0.350	0.082	118.440	2.433
ECPA-12A	13.948	148.522	0.458	0.031	74.940	2.949
ECPA-12B	14.103	146.292	0.419	0.029	123.040	3.280
ECPA-12C	13.488	85.416	0.762	0.032	136.700	4.118
ECPA-12D	13.507	79.200	0.648	0.023	66.240	3.470
ECPA-13A	5.071	59.816	0.949	0.042	33.010	7.444

ECPA-13B	5.180	42.002	0.834	0.027	23.600	12.516
ECPA-13C	6.575	0.812	10.000	0.011	11.200	26.874
ECPA-13D	5.747	0.989	5.872	0.120	14.020	7.063
ECPA-14A	13.754	258.573	0.459	0.048	249.670	2.143
ECPA-14B	13.707	237.099	0.510	0.029	65.290	2.253
ECPA-14C	13.936	254.320	0.411	0.027	96.540	3.197
ECPA-14D	13.519	257.875	0.395	0.079	147.020	2.587
ECPA-23A	66.347	103.439	2.157	0.000	4.700	8.910
ECPA-23B	76.427	76.082	0.231	0.193	3.100	8.788
ECPA-23C	40.948	33.844	7.624	0.025	9.140	9.123
ECPA-24A	11.941	286.078	6.565	0.500	182.650	3.180
ECPA-24B	10.903	1513.689	10.000	0.000	174.340	7.675
ECPA-24C	10.874	1519.411	1.554	0.500	157.550	14.837
ECPA-24D	11.582	2546.101	0.010	0.500	360.750	5.439
ECPA-25A	10.807	109.623	0.257	0.015	176.590	1.740
ECPA-27A	7.761	0.744	6.737	0.082	5.330	5.452
ECPA-27B	6.771	0.247	9.997	0.078	3.110	32.890
ECPA-27C	8.633	16.718	8.087	0.000	7.960	16.954
ECPA-27D	7.464	0.266	10.000	0.094	2.540	35.449
ECPA-28A	29.494	0.851	10.000	0.007	13.080	22.871
ECPA-28B	35.217	18.930	0.330	0.014	13.940	11.262
ECPA-28C	23.732	5.749	2.776	0.017	43.520	10.751
ECPA-28D	30.152	10.728	1.425	0.033	36.340	3.261
ECPA-28E	26.960	3.587	1.794	0.024	73.550	1.721
ECPA-28F	24.959	46.381	3.161	0.025	51.340	4.395
ECPA-28G	26.562	65.851	2.155	0.020	107.750	5.365
ECPA-28H	26.031	35.051	1.759	0.017	79.390	2.718
ECPA-28I	26.628	103.110	2.054	0.012	153.610	3.071
ECPA-28J	26.716	11.869	1.089	0.038	70.910	4.190
ECPA-28K	26.563	30.224	1.879	0.032	117.370	2.396
ECPA-28L	27.499	4.903	10.000	0.021	39.950	4.660
ECPA-28M	29.318	9.798	1.101	0.010	38.570	7.189
ECPA-30A	74.963	261.622	1.836	0.004	9.410	26.716
ECPA-30B	65.547	207.185	0.849	0.018	13.050	10.021
ECPA-30C	60.402	336.028	10.000	0.000	38.750	9.408
ECPA-30D	62.758	300.210	0.759	0.008	27.420	8.296
ECPA-30E	46.914	231.081	0.721	0.026	16.790	20.181
ECPA-30F	57.029	323.445	0.518	0.023	20.770	11.476
ECPA-32A	2.186	14.161	1.458	0.027	20.640	9.514
ECPA-32B	2.744	41.476	4.754	0.000	19.640	9.700
ECPA-32C	1.920	28.799	0.648	0.014	48.580	1.505
ECPA-33A	154.635	1008.782	0.598	0.007	34.840	10.269
ECPA-33B	112.408	1173.184	0.538	0.013	34.320	12.780
ECPA-33C	122.097	927.169	0.400	0.012	24.900	17.513
ECPA-33D	59.879	907.502	0.685	0.007	231.680	6.166
ECPA-34A	11.579	274.396	0.249	0.038	15.180	10.662
ECPA-34B	9.209	238.626	0.403	0.017	19.680	15.568
ECPA-34C	10.544	44.929	0.893	0.018	12.780	16.552
ECPA-34D	10.393	30.394	1.178	0.025	34.260	6.616
ECPA-34E	10.050	31.024	0.514	0.025	17.670	5.761
ECPA-35A	4.058	565.533	0.938	0.011	7.140	12.690
ECPA-35B	4.005	488.846	0.921	0.014	7.840	9.553

ECPA-35C	2.312	51.461	0.932	0.006	13.280	23.970
ECPA-35D	2.711	48.037	0.964	0.008	13.370	22.179
ECPA-35E	2.566	53.841	0.928	0.011	56.200	10.911
ECPA-35F	2.787	54.318	0.921	0.012	55.910	10.653
ECPA-38A	0.871	43.165	10.000	0.000	11.030	12.642
ECPA-38B	0.738	10.110	0.285	0.148	12.360	11.695
ECPA-38C	1.068	127.446	10.000	0.000	11.620	25.176
ECPA-38D	0.878	146.272	0.481	0.014	12.400	5.994
ECPA-38E	0.788	12.830	0.163	0.082	19.050	3.582
ECPA-38F	0.789	1.572	5.463	0.184	15.170	5.918
ECPA-38G	0.834	99.730	10.000	0.001	14.370	10.818
ECPA-38H	1.000	20.542	0.445	0.037	9.590	15.447
ECPA-38I	0.816	27.284	0.632	0.208	17.050	7.013
ECPA-38J	0.932	17.568	8.501	0.000	14.140	10.623
ECPA-38K	0.776	42.652	1.368	0.046	7.560	16.954
ECPA-38L	0.923	19.992	0.210	0.062	14.370	6.526
ECPA-38M	0.679	5.133	0.459	0.043	14.840	11.006
ECPA-38N	0.927	15.572	0.317	0.043	15.040	8.012
ECPA-38O	0.885	20.352	0.924	0.055	11.300	8.596
ECPA-38P	0.834	4.319	1.766	0.055	13.130	13.821
ECPA-41A	1.208	90.015	4.725	0.005	175.170	1.219
ECPA-41B	1.239	139.384	2.220	0.019	157.190	6.551
ECPA-42A	1.929	25.920	0.516	0.028	58.840	2.945
ECPA-42B	2.234	27.693	0.503	0.011	72.720	2.205
ECPA-42C	2.171	15.593	0.599	0.019	57.830	2.171
ECPA-43A	14.503	66.410	6.581	0.000	30.640	8.551
ECPA-43B	12.183	2.100	3.043	0.002	37.700	11.057
ECPA-43C	17.860	82.442	0.010	0.000	31.500	11.557
ECPA-43D	15.282	79.070	10.000	0.000	20.030	20.522
ECPA-44A	0.702	34.720	0.804	0.019	145.560	2.306
ECPA-44B	0.775	7.983	10.000	0.001	99.950	2.591

Appendix 5: Fitted parameters of SorpKinAnalysis 1.0

Table A 2: Fitted parameters of SorpKinAnalysis 1.0.

ID	initial mass	equilibrium $K_{f,oc}$	f_{NE}	k_{des}	$DegT_{50eq}$	Chi²-error
ECPA-01A	7.343	9.093	0.583	0.050	79.490	2.824
ECPA-01B	6.901	12.652	0.462	0.078	93.600	4.983
ECPA-01C	7.512	8.367	0.440	0.043	60.660	1.914
ECPA-01D	7.192	9.417	0.514	0.048	142.580	2.166
ECPA-02A	31.799	14.100	10.000	0.000	12.080	6.282
ECPA-02B	34.074	11.819	10.000	0.000	4.990	26.780
ECPA-02C	36.290	56.703	0.186	0.037	4.290	10.874
ECPA-02D	29.809	12.904	10.000	0.000	10.260	9.106
ECPA-02E	26.615	4.887	63.800	0.000	21.170	7.006
ECPA-03A	18.519	60.262	0.703	0.017	30.960	4.633
ECPA-03B	17.709	41.406	0.401	0.060	46.900	3.854
ECPA-03C	17.339	114.636	0.905	0.019	14.550	10.008
ECPA-03D	18.290	48.666	0.361	0.036	53.050	2.725
ECPA-04A	10.255	34.999	0.437	0.048	145.770	1.052
ECPA-04B	10.203	32.238	0.183	0.086	128.080	1.945

ECPA-04C	10.270	41.717	0.476	0.053	145.420	1.006
ECPA-04D	10.226	45.475	0.317	0.045	173.140	1.226
ECPA-05A	7.314	2.436	0.523	0.013	140.840	0.844
ECPA-05B	7.001	0.443	2.060	0.016	156.100	1.581
ECPA-05C	7.381	3.718	0.341	0.012	64.940	1.129
ECPA-05D	7.395	1.118	37.100	0.000	117.530	2.279
ECPA-06A	67.158	341.733	0.715	0.041	108.280	1.552
ECPA-06B	62.299	302.583	0.612	0.027	90.080	2.071
ECPA-06C	66.298	380.357	0.613	0.052	176.810	2.430
ECPA-06D	65.331	316.360	0.672	0.034	77.420	1.010
ECPA-07A	45.367	74.214	0.753	0.032	55.670	3.469
ECPA-07B	47.041	81.276	0.314	0.037	45.410	2.317
ECPA-07C	46.884	106.479	0.699	0.036	81.050	2.469
ECPA-07D	45.771	69.425	0.474	0.028	50.160	1.908
ECPA-08A	12.026	151.842	0.390	0.022	98.690	5.764
ECPA-08B	12.295	113.379	0.495	0.017	104.870	4.867
ECPA-09A	2.818	3529.649	0.318	0.498	98.930	3.785
ECPA-09B	2.805	3155.046	0.193	0.500	79.500	1.877
ECPA-09C	2.725	3567.394	0.262	0.500	43.540	2.199
ECPA-09D	2.731	1901.560	0.244	0.500	55.440	2.315
ECPA-11A	69.483	206.740	0.540	0.025	156.670	2.137
ECPA-11B	69.715	256.214	0.550	0.025	157.880	2.782
ECPA-11C	69.342	273.047	0.469	0.023	236.550	2.975
ECPA-11D	70.164	193.111	0.582	0.021	112.700	3.751
ECPA-11E	65.124	192.973	0.524	0.021	153.080	3.948
ECPA-11F	62.757	188.537	0.491	0.037	304.520	1.545
ECPA-11G	66.362	227.093	0.470	0.038	170.280	2.014
ECPA-11H	63.487	160.383	0.350	0.083	118.240	2.433
ECPA-12A	13.949	148.587	0.457	0.031	74.950	2.949
ECPA-12B	14.106	146.380	0.418	0.029	123.010	3.281
ECPA-12C	13.489	85.483	0.761	0.032	136.720	4.118
ECPA-12D	13.507	79.242	0.647	0.023	66.250	3.469
ECPA-13A	5.072	59.829	0.948	0.042	33.010	7.447
ECPA-13B	5.180	42.036	0.834	0.027	23.610	12.517
ECPA-13C	6.576	0.812	10.000	0.011	11.200	26.874
ECPA-13D	5.746	0.062	94.000	0.119	13.990	7.023
ECPA-14A	13.754	258.613	0.459	0.048	249.810	2.142
ECPA-14B	13.709	237.174	0.510	0.029	65.290	2.255
ECPA-14C	13.934	254.286	0.411	0.026	96.550	3.198
ECPA-14D	13.519	257.888	0.394	0.079	147.010	2.588
ECPA-23A	66.372	103.586	0.990	0.000	4.700	8.120
ECPA-23B	76.545	76.149	0.232	0.193	3.100	8.017
ECPA-23C	40.920	33.946	7.610	0.025	9.150	8.462
ECPA-24A	11.912	691.101	2.300	0.500	450.240	2.895
ECPA-24B	10.903	1513.878	7.250	0.000	174.360	7.259
ECPA-24C	10.924	59.522	28.100	0.488	17.700	13.494
ECPA-24D	11.581	2572.148	0.006	0.279	364.560	4.956
ECPA-25A	10.807	109.635	0.257	0.015	176.630	1.544
ECPA-27A	7.776	0.071	67.600	0.084	5.270	4.829
ECPA-27B	6.782	0.038	63.900	0.078	3.090	12.434
ECPA-27C	8.630	16.647	62.000	0.000	7.960	15.461
ECPA-27D	7.486	0.005	571.000	0.094	2.530	14.546

ECPA-28A	29.487	0.851	10.000	0.007	13.080	21.633
ECPA-28B	35.236	18.952	0.329	0.014	13.940	10.448
ECPA-28C	23.776	1.334	10.300	0.018	42.060	10.225
ECPA-28D	30.150	10.758	1.420	0.033	36.360	3.023
ECPA-28E	26.963	3.603	1.790	0.024	73.540	1.594
ECPA-28F	24.960	46.467	3.160	0.024	51.360	4.076
ECPA-28G	26.595	482.966	0.000	0.492	242.580	14.605
ECPA-28H	26.032	35.099	1.760	0.017	79.390	2.522
ECPA-28I	30.884	303.018	0.000	0.500	103.860	14.792
ECPA-28J	26.719	11.897	1.090	0.038	70.920	3.886
ECPA-28K	26.564	30.274	1.880	0.032	117.460	2.221
ECPA-28L	27.591	0.124	311.000	0.022	38.650	4.189
ECPA-28M	29.318	9.815	1.100	0.010	38.580	6.667
ECPA-30A	75.628	268.420	1.780	0.004	9.420	25.067
ECPA-30B	65.560	207.259	0.849	0.018	13.050	9.401
ECPA-30C	60.415	336.113	10.000	0.000	25.640	8.578
ECPA-30D	62.762	300.255	0.759	0.008	27.430	7.776
ECPA-30E	47.025	231.747	0.721	0.026	16.790	18.911
ECPA-30F	57.072	324.015	0.517	0.023	20.780	10.762
ECPA-32A	2.186	14.168	1.460	0.027	20.630	8.441
ECPA-32B	2.745	41.458	52.100	0.000	19.630	8.600
ECPA-32C	1.919	28.840	0.648	0.014	48.610	1.334
ECPA-33A	154.855	1010.944	0.596	0.007	34.840	10.276
ECPA-33B	113.053	1175.490	0.536	0.013	34.140	11.870
ECPA-33C	122.737	931.194	0.397	0.012	24.860	16.251
ECPA-33D	59.959	909.136	0.680	0.007	230.760	5.718
ECPA-34A	11.569	274.533	0.248	0.037	15.210	10.659
ECPA-34B	9.208	238.660	0.403	0.017	19.690	15.571
ECPA-34C	10.516	44.715	0.896	0.018	12.840	16.545
ECPA-34D	10.392	30.407	1.180	0.025	34.270	6.611
ECPA-34E	10.050	31.090	0.514	0.025	17.670	5.762
ECPA-35A	4.080	508.394	0.940	0.013	6.830	14.418
ECPA-35B	4.006	489.168	0.920	0.014	7.840	9.551
ECPA-35C	2.673	87.158	0.673	0.005	14.000	27.467
ECPA-35D	3.103	86.729	0.604	0.007	14.590	24.974
ECPA-35E	2.566	53.864	0.928	0.011	56.210	10.914
ECPA-35F	2.786	54.344	0.920	0.012	55.920	10.655
ECPA-38A	0.870	43.078	175.000	0.000	11.040	12.607
ECPA-38B	0.738	10.319	0.272	0.140	12.420	11.692
ECPA-38C	1.067	127.452	39.800	0.000	11.630	25.169
ECPA-38D	0.878	146.284	0.480	0.014	12.390	5.985
ECPA-38E	0.788	12.800	0.165	0.083	19.030	3.578
ECPA-38F	0.789	1.409	6.120	0.184	15.140	5.915
ECPA-38G	0.831	99.720	258.000	0.000	14.460	10.721
ECPA-38H	1.000	20.533	0.445	0.036	9.590	15.449
ECPA-38I	0.816	27.304	0.631	0.207	17.060	7.011
ECPA-38J	0.932	17.573	5.820	0.000	14.140	10.618
ECPA-38K	0.775	42.957	1.360	0.045	7.590	16.951
ECPA-38L	0.923	19.992	0.210	0.061	14.370	6.524
ECPA-38M	0.680	5.106	0.462	0.044	14.810	11.002
ECPA-38N	0.928	15.581	0.317	0.043	15.040	8.004
ECPA-38O	0.885	20.366	0.923	0.054	11.300	8.597

ECPA-38P	0.827	2.184	3.310	0.054	12.960	13.791
ECPA-41A	1.208	90.017	4.720	0.005	175.030	1.214
ECPA-41B	1.257	135.246	2.230	0.021	135.500	6.575
ECPA-42A	1.929	25.909	0.516	0.028	58.830	2.946
ECPA-42B	2.234	27.634	0.501	0.011	72.640	2.203
ECPA-42C	2.172	15.591	0.599	0.019	57.800	2.171
ECPA-43A	15.049	55.909	0.155	0.047	27.740	8.892
ECPA-43B	12.167	2.050	4.780	0.001	37.790	11.059
ECPA-43C	17.855	82.416	0.000	0.499	31.500	11.554
ECPA-43D	15.282	79.093	25.400	0.000	20.040	20.519
ECPA-44A	0.702	34.742	0.804	0.019	145.540	2.306
ECPA-44B	0.775	8.099	90.500	0.000	100.610	2.501