R_s - K estimation template manual

Template version 1
2020-02-29

Cite as: PaSOC, 2020. Rs - K estimation template. Version 1. https://pasoc.eu/passive-sampling-rate-model-fit/

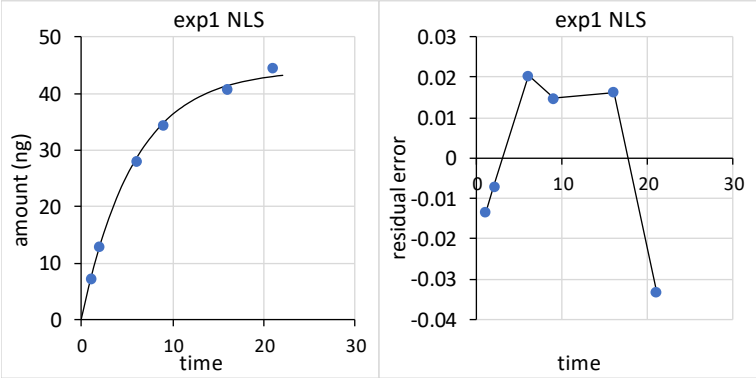

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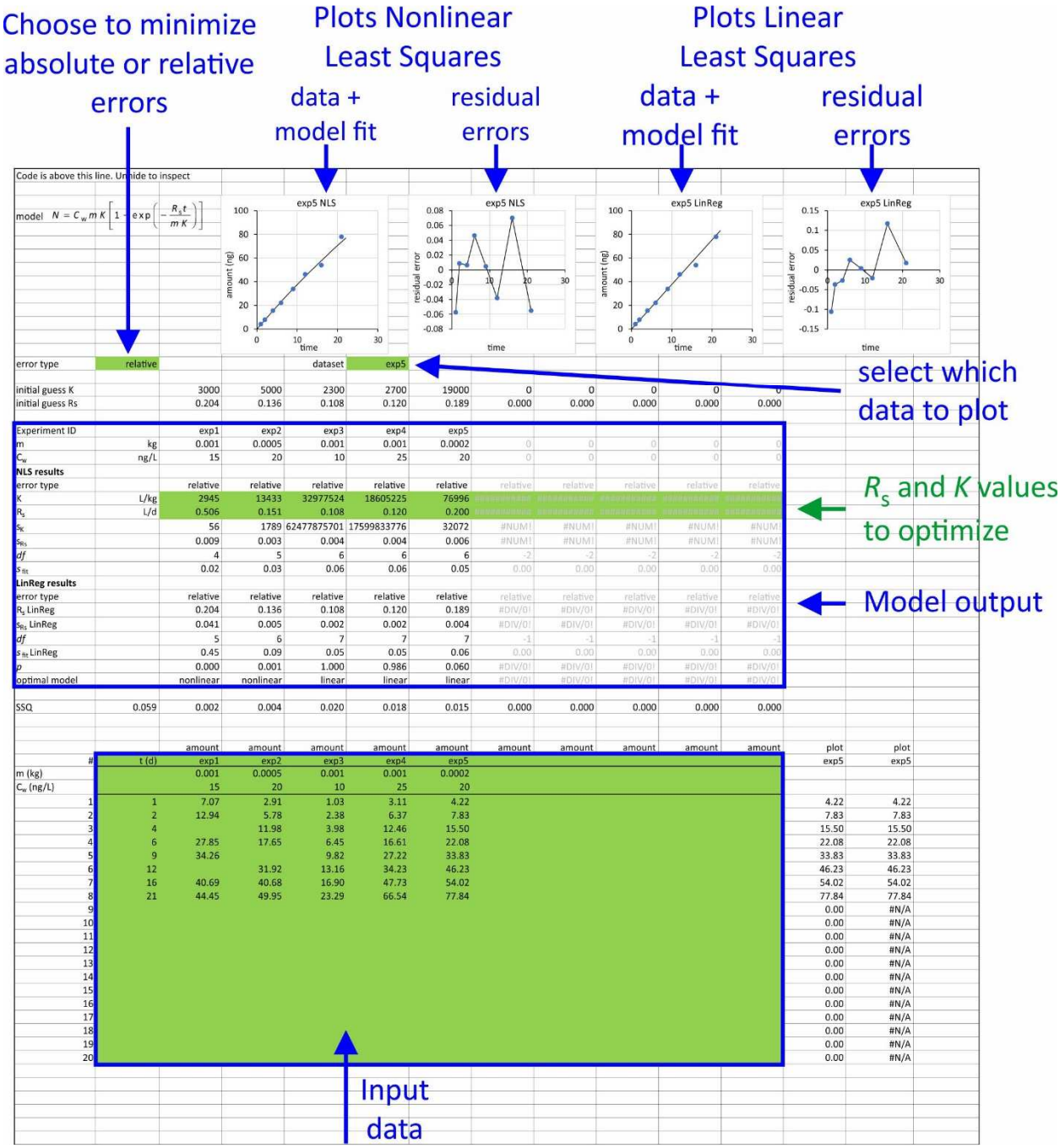
Table of Contents

1. Overview of worksheet “Rs-K model”

Structure of the worksheet is as follows.

- Top: Plots with results of nonlinear and linear least squares analysis
- Middle: Results of of nonlinear and linear least squares analysis
- Bottom: input data

Green cells can be safely changed. Do not change the other cells.
Code is hidden at the top for convenience. Unhide rows if you want to see it.



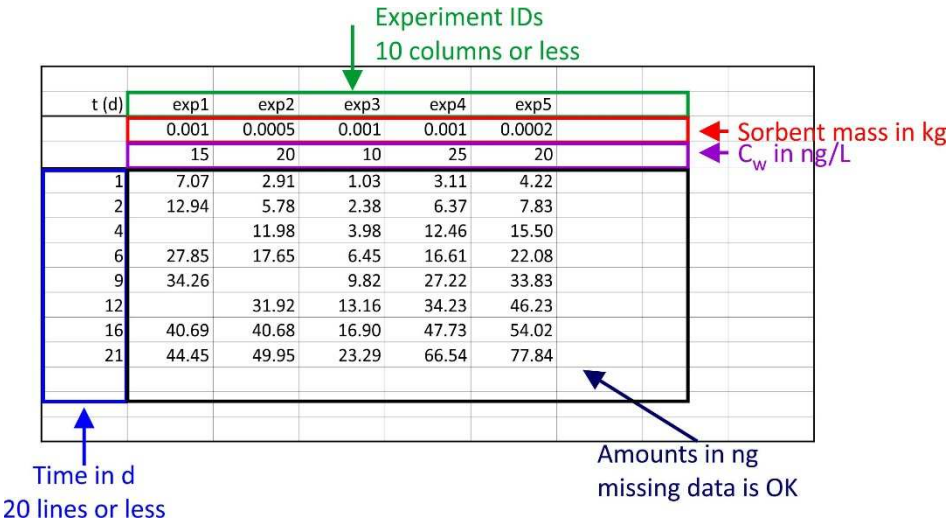
2. Overview of procedure

1. Enter input data (type or paste as values)
2. Specify initial guess of R_s and K
3. Run Solver
4. Inspect the plots for each data set
5. Inspect the numerical results

2.1. Enter input data

Two ways to go:

1. type data directly in the Input data block
2. prepare a data block separately and paste as follows:

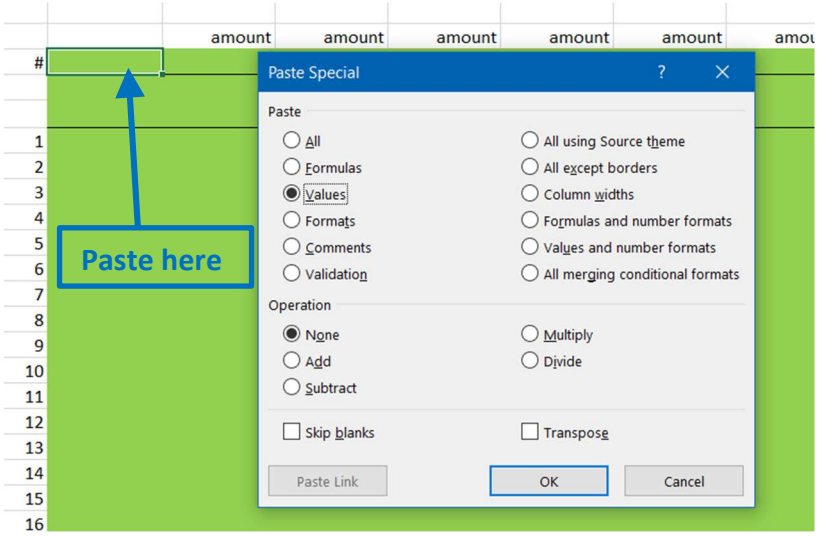


t (d)	exp1	exp2	exp3	exp4	exp5
	0.001	0.0005	0.001	0.001	0.0002
	15	20	10	25	20
1	7.07	2.91	1.03	3.11	4.22
2	12.94	5.78	2.38	6.37	7.83
4		11.98	3.98	12.46	15.50
6	27.85	17.65	6.45	16.61	22.08
9	34.26		9.82	27.22	33.83
12		31.92	13.16	34.23	46.23
16	40.69	40.68	16.90	47.73	54.02
21	44.45	49.95	23.29	66.54	77.84

Copy data

t (d)	exp1	exp2	exp3	exp4	exp5
	0.001	0.0005	0.001	0.001	0.0002
	15	20	10	25	20
1	7.07	2.91	1.03	3.11	4.22
2	12.94	5.78	2.38	6.37	7.83
4		11.98	3.98	12.46	15.50
6	27.85	17.65	6.45	16.61	22.08
9	34.26		9.82	27.22	33.83
12		31.92	13.16	34.23	46.23
16	40.69	40.68	16.90	47.73	54.02
21	44.45	49.95	23.29	66.54	77.84

Paste as values

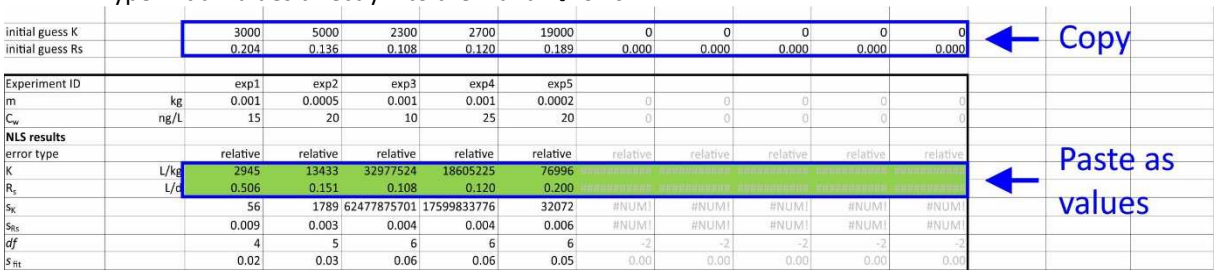


Never use cut and paste, as this invalidates cell references in the worksheet.

2.2. Specify initial guess of R_s and K

NLS parameter estimation need an initial guess of the values. Initial values are not too critical, but extremely high values and zeros should be avoided.
Just below the plots are two rows with fair guesses.
Two ways to go:

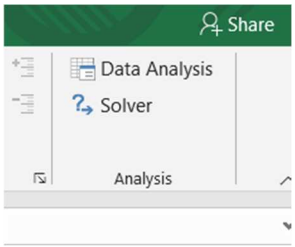
1. Copy the suggested guesses and past as values in the K and R_s row below that.
2. Type initial values directly into the K and R_s rows



initial guess K		3000	5000	2300	2700	19000	0	0	0	0	0
initial guess Rs		0.204	0.136	0.108	0.120	0.189	0.000	0.000	0.000	0.000	0.000
Experiment ID		exp1	exp2	exp3	exp4	exp5					
m	kg	0.001	0.0005	0.001	0.001	0.0002	0	0	0	0	0
C_w	ng/L	15	20	10	25	20	0	0	0	0	0
NLS results											
error type		relative	relative	relative	relative	relative	relative	relative	relative	relative	relative
K	L/kg	2945	13433	32977524	18605225	76996	##########	##########	##########	##########	##########
R_s	L/d	0.506	0.151	0.108	0.120	0.200	##########	##########	##########	##########	##########
s_K		56	1789	62477875701	17599833776	32072	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
s_{Rs}		0.009	0.003	0.004	0.004	0.006	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!
df		4	5	6	6	6	-2	-2	-2	-2	-2
s_{fit}		0.02	0.03	0.06	0.06	0.05	0.00	0.00	0.00	0.00	0.00

2.3. Run Solver

Check if Solver is activated (far right on the Data tab)

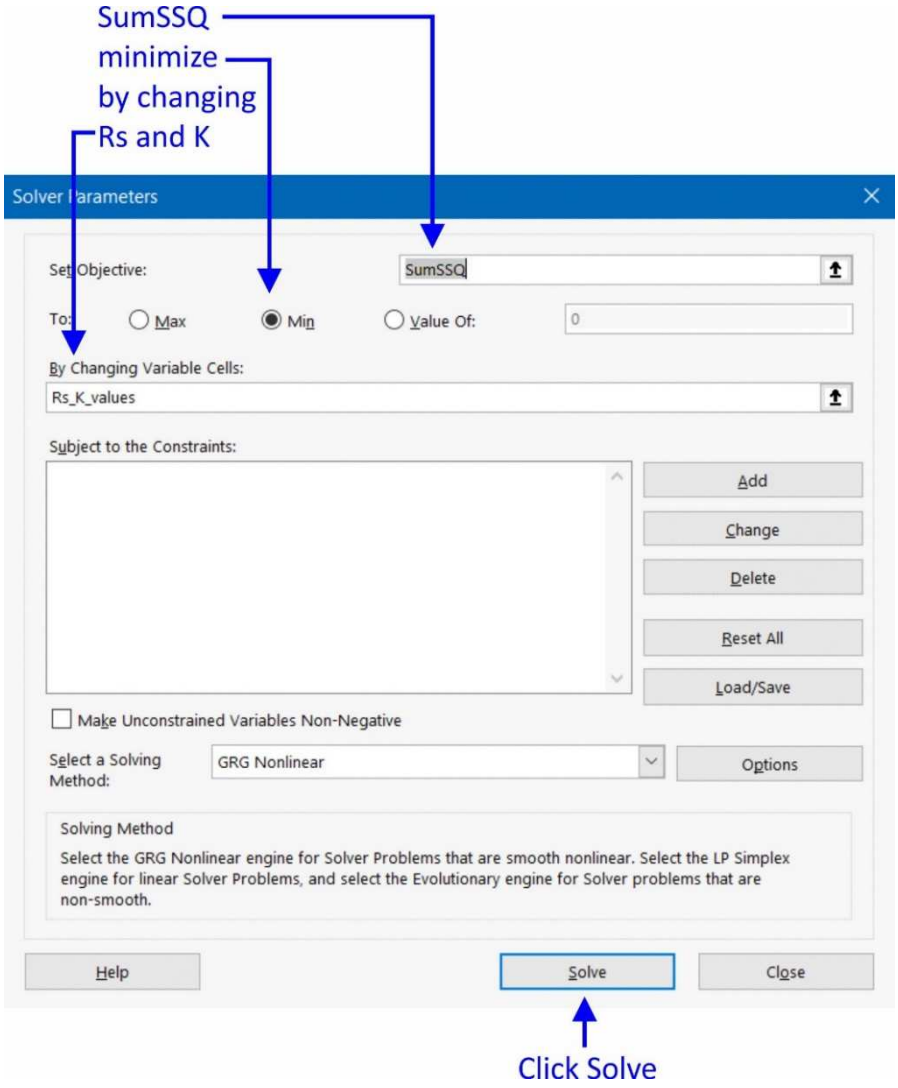


If Solver is not loaded then load it (once and forever)

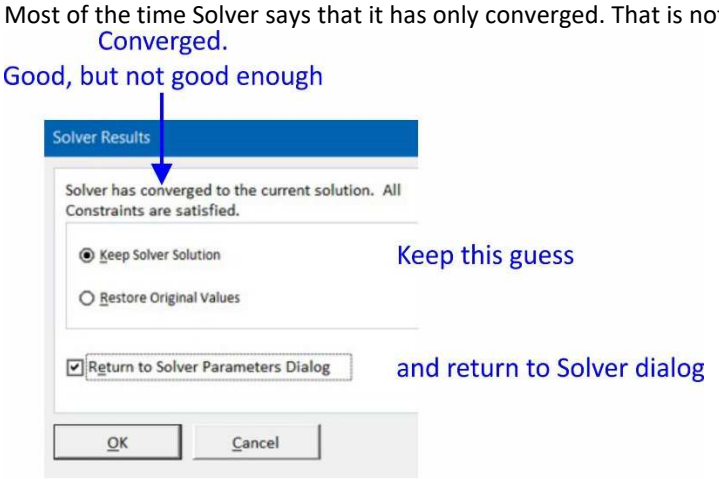
1. go to section 4 Appendix: Load Solver
2. or go to https://support.office.com/en-us/article/load-the-solver-add-in-in-excel-612926fc-d53b-46b4-872c-e24772f078ca
3. or watch https://www.youtube.com/watch?v=W6tIS4JZ5J0

Click Solver (far right on the Data tab)
Check:

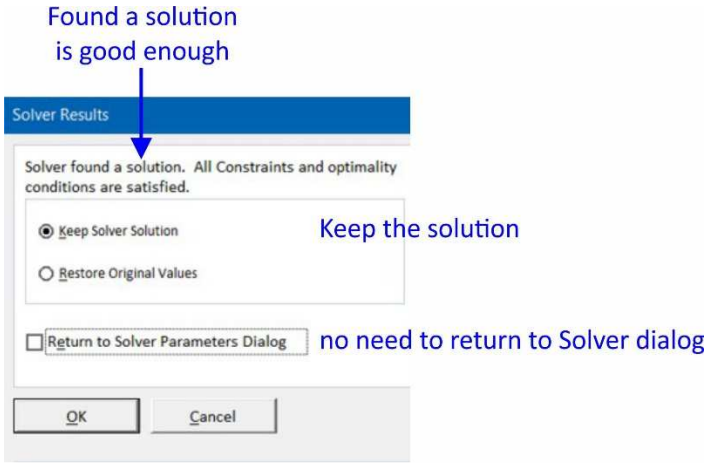
- Objective : SumSSQ
- To : Min
- By Changing Variable Cells : Rs_K_values



Most of the time Solver says that it has only converged. That is not good enough.



Return to the Solver dialog and click Solve again, (2-4 times) until Solver says that it has “found a solution”


Found a solution
is good enough
Solver Results
Solver found a solution. All Constraints and optimality conditions are satisfied.
Keep Solver Solution
Restore Original Values
Keep the solution
Return to Solver Parameters Dialog
no need to return to Solver dialog
OK
Cancel

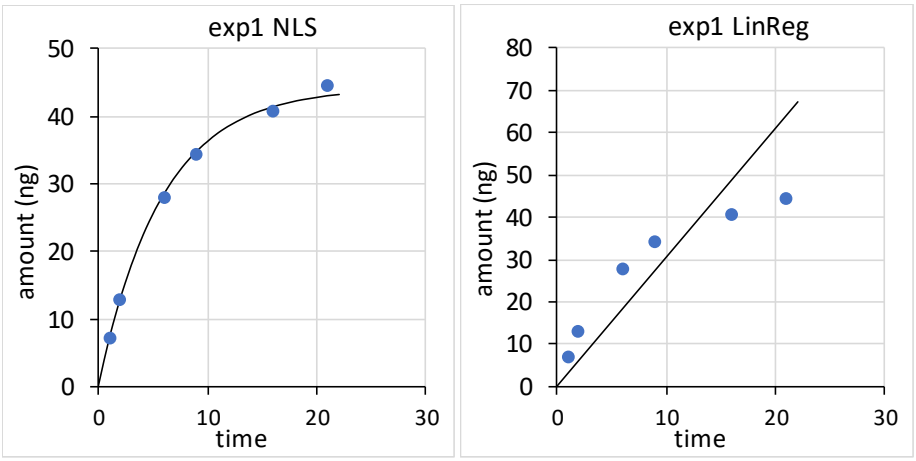
2.4. Inspect the plots for each data set

Select the data ID from the green drop-down list just below the plots.
Unit for the vertical axes of the residual error plots depends on the chosen error type:

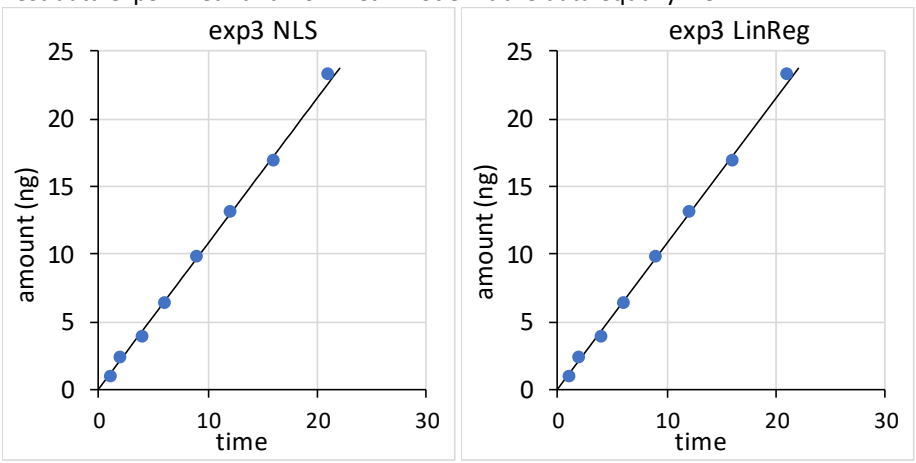
- ng if absolute errors are minimized: modeled - measured.
- relative difference if relative errors are minimized: (modeled - measured)/measured.

The nonlinear model always gives a better fit of the data (1 more adjustable parameter), but not always significantly so (see section 2.5).

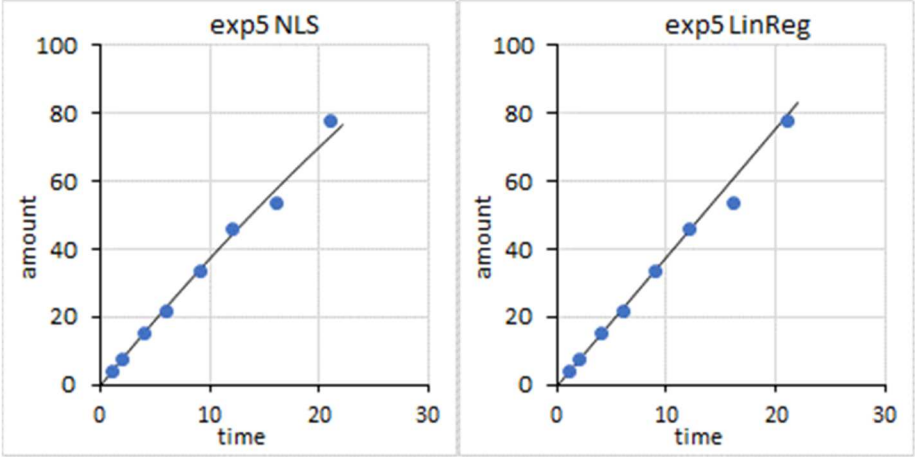
Test data exp1: nonlinear model is clearly better



Test data exp3: linear and nonlinear model fit the data equally well.



Test data exp5: Nonlinear model seems to fit the data slightly better, but maybe not significantly so.



2.5. Inspect the numerical results

Meaning of the entries in this table are as follows:

NLS results	
error type	absolute or relative errors, as chosen
K	estimated K
R_s	estimated R_s
s_K	estimated standard error of K
s_{Rs}	estimated standard error of R_s
df	degrees of freedom (number of data points minus 2)
s_{fit}	standard deviation of residual errors. In ng if absolute errors are minimized Given as a fraction if relative errors are minimized
LinReg results	
error type	absolute or relative errors, as chosen
R_s LinReg	estimated R_s
s_{Rs} LinReg	estimated standard error of R_s
df	degrees of freedom (number of data points minus 1)
s_{fit} LinReg	standard deviation of residual errors. In ng if absolute errors are minimized Given as a fraction if relative errors are minimized
p	Probability that the nonlinear model gives a better fit by chance. Value is based on partial F-test; https://www.youtube.com/watch?v=G_obrpV70QQ. See examples on next page.
optimal model	nonlinear if $p < 0.05$; linear if $p \geq 0.05$

See examples on next page.

Some examples based on test data (xlsx file, worksheet “test data”)

	exp1	exp3	exp5
NLS results			
error type	relative	relative	relative
K	2945	7.8E07	76997
R_s	0.506	0.108	0.200
s_K	56	3.5E11	32073
s_{Rs}	0.009	0.004	0.006
df	4	6	6
s_{fit}	0.02	0.06	0.05
LinReg results			
error type	relative	relative	relative
R_s LinReg	0.204	0.108	0.189
s_{Rs} LinReg	0.041	0.002	0.004
df	5	7	7
s_{fit} LinReg	0.45	0.05	0.06
p	0.000	1.000	0.060
optimal model	nonlinear	linear	linear

exp1
Nonlinear model yields $K = 2945 \pm 56$ L/kg, $R_s = 0.506 \pm 0.009$, residual standard error = 0.02.
Performance of the linear model is worse: residual standard error = 0.45
Probability that the nonlinear model accidentally gives a better fit is < 0.001.
Nonlinear model is selected.

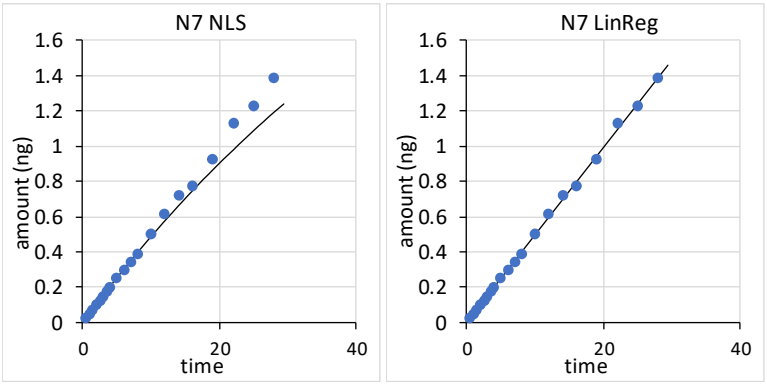
exp3
Nonlinear model yields $K = 7.8 \cdot 10^7 \pm 3.5 \cdot 10^{11}$ L/kg, $R_s = 0.108 \pm 0.004$ L/d, residual standard error = 0.06.
Linear model describes the data equally well: $R_s = 0.108 \pm 0.002$ L/d, residual standard error = 0.05.
Probability that the nonlinear model accidentally gives a better fit is 1. There is no added value in using the nonlinear model. This is also evidenced by the huge standard error in K.
Linear model is selected

exp5
Nonlinear model yields $K = 77{,}000 \pm 32{,}000$ L/kg, $R_s = 0.200 \pm 0.006$ L/d, residual standard error = 0.05
Linear model describes the data equally well: $R_s = 0.189 \pm 0.004$ L/d, residual standard error = 0.06.
Probability that the nonlinear model accidentally gives a better fit is 0.06. This is higher than the 0.05 threshold.
There is not sufficient reason to assume that the nonlinear model gives a better fit.
Linear model is selected.

3. Known issues

Model lines not visible in the plots
Cause: initial values were set to zero. Use nonzero initial values (section 2.2)

Nonlinear model seems to give worse results than linear model.
Like this:



Cause: Optimization is not yet complete: Solver has only "converged to the current solution". Run Solver again until "Solver has found a solution" (section 2.3).

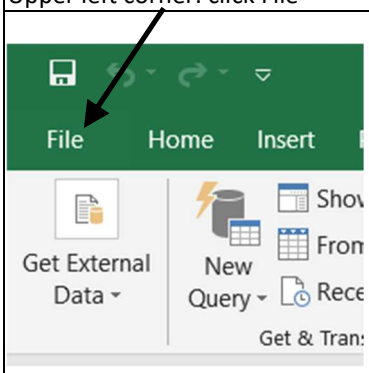
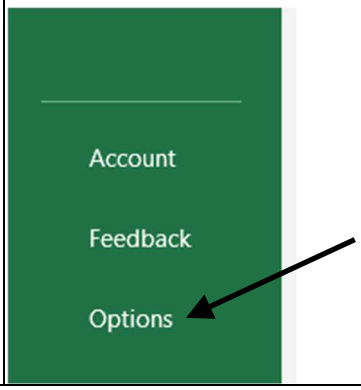
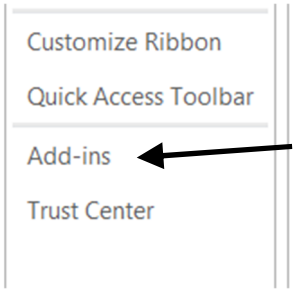
Message "Objective cell contents must be a formula"
Cause: with the Solver dialog open, an empty cell was accidentally selected before clicking the Solve button. Check the "Set objective" reference in the solver dialog. Change this to "SumSSQ".

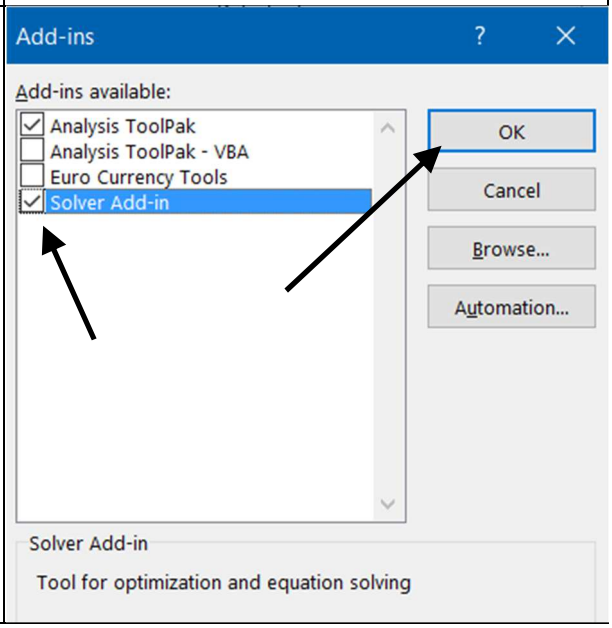
Message "Solver has found a solution" but the model fits are very poor.
Cause: with the Solver dialog open, a non-empty cell was accidentally selected before clicking the Solve button. Check the "Set objective" reference in the solver dialog. Change this to "SumSSQ".

Message "Objective cell values do not converge"
Cause: with the Solver dialog open, a non-empty cell was accidentally selected before clicking the Solve button. Check the "Set objective" reference in the solver dialog. Change this to "SumSSQ".

Other unexpected results
Send an e-mail when you run into unexpected results (keesbooij@pasoc.eu). Attach a copy of the workbook.

4. Appendix: Load Solver Add-in

Step 1	Step 2	Step 3
Upper left corner: click File	Lower left corner: click Options	Click Add-ins
		

Step 4	Step 5
Bottom: select Excel Add-ins and Go	Check Solver Add-in and click OK
	

Done