Template for estimating diffusion coefficients with film stacking method

Background information and manual

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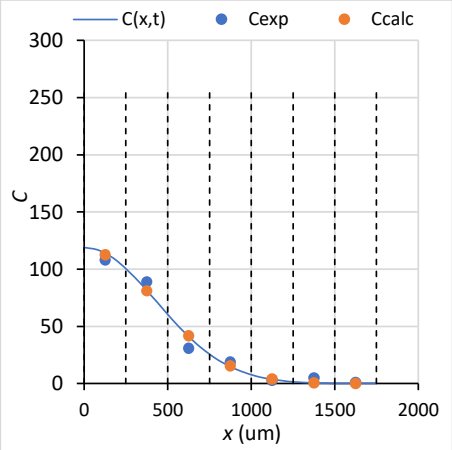

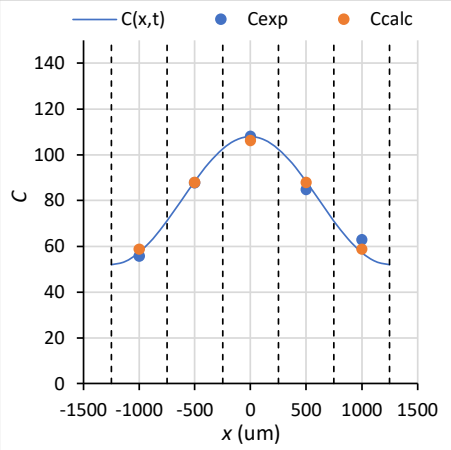

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Table of Contents

Abstract

This document provides background information and instructions for use of the Excel template for estimating diffusion coefficients with the film stacking method. The template can be used for configurations with a single spiked sheet in the middle or on top of a stack of unspiked films of equal thickness. The template yields best estimates of the logarithm of the diffusion coefficient and its standard error. Graphical output of residual errors and model fit is also provided.

Templates for single or multiple spiked sheets in any position in the stack are available on request.

1. Scientific background

Film stacking is a well established technique for estimating diffusion coefficients (D_s) in sorbent films (Belles et al., 2018; Narváez Valderrama et al., 2016; Pintado-Herrera et al., 2016; Rusina et al., 2010; Verhagen et al., 2019). With this method a spiked polymer sheet is brought in contact with a number of unspiked sheets for some time. The position of the spiked sheet is usually either at the top or in the middle of the stack. The diffusion coefficient is then determined by fitting the concentrations in the individual sheets to an appropriate diffusion model that is based on integration of Fick's second law under the boundary conditions that the flux at the stack boundaries equals zero.

Three models have been used to estimate D_s. Rusina et al. (2010) and Verhagen et al. (2019) applied an explicit numerical integration scheme. This method is described in best detail by Verhagen et al. (2019). Crank (1975) gives two analytical solutions. The first is an infinite series of cosines and exponentials (Crank's equation 4.56), which was used by Belles et al. (2018). The second is an infinite series of error functions (Crank's equation 2.17), which was used by Narváez Valderrama et al. (2016) and Pintado-Herrera et al. (2016). For a system with one spiked sheet in the center of the stack the concentrations $C(x,t)$ are given by

$$\frac{2C(x,t)}{C_0} = \sum_{n=-\infty}^{\infty} \mathrm{erf}\left(\frac{x_1 + 2n\ell - x}{\sqrt{4D_s t}}\right) + \mathrm{erf}\left(\frac{x_1 - 2n\ell + x}{\sqrt{4D_s t}}\right) \qquad 1$$

where C_0 is the initial concentration in the spiked sheet, x is the distance from the center of the stack, x_1 is the half-thickness of the spiked sheet, and ℓ is the half-thickness of the stack (Figure 1, left panel). Equation 1 can also be used for a stack configuration with a spiked sheet at the top, but here x_1 and ℓ represent the full thickness of spiked sheet and stack (Figure 1, right panel).

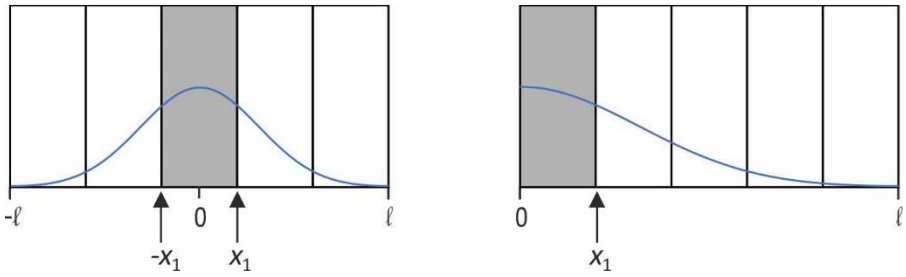


Figure 1. Coordinates used in equation 1 for film stacks with a spiked sheet in the center (left) and at the top (right). Blue lines show the local concentrations after some time.

Model values of the average concentration in a particular sheet can be obtained by integrating equation 1 between the sheet boundaries and dividing by the sheet thickness, noting that the antiderivative of erf(y) equals y erf(y) + exp(-y^2)/$\sqrt{\pi}$. Diffusion coefficients can then be estimated by nonlinear least squares regression.

For practical reasons the the summation in equation 1 has to run over finite values of n. Truncation errors increase with time, but for very long incubation times the concentrations in individual sheets become analytically indistinguishable. Differences in concentrations are less than 1% when $D_s t/\ell^2 > 0.6$, which precludes D_s estimation anyway. Relative truncation errors for shorter incubation times are smaller than 10^{-7} when n runs between −3 and +3. In present template four additional terms are included (n between −5 and +5).

Optimization of logD_s is done with the Excel Solver Add-in. Estimation of its standard error is done by numerical differentiation as described by Billo (2001).

With present template, diffusion coefficients can be estimated for configurations with stacks of sheets of equal thickness and a single spiked sheet in the center or at the top. PaSOC has more general templates available for configurations with single or multiple spiked sheets in any position in the stack. Contact info@pasoc.eu for details.

2. Use of the D_s calculation template

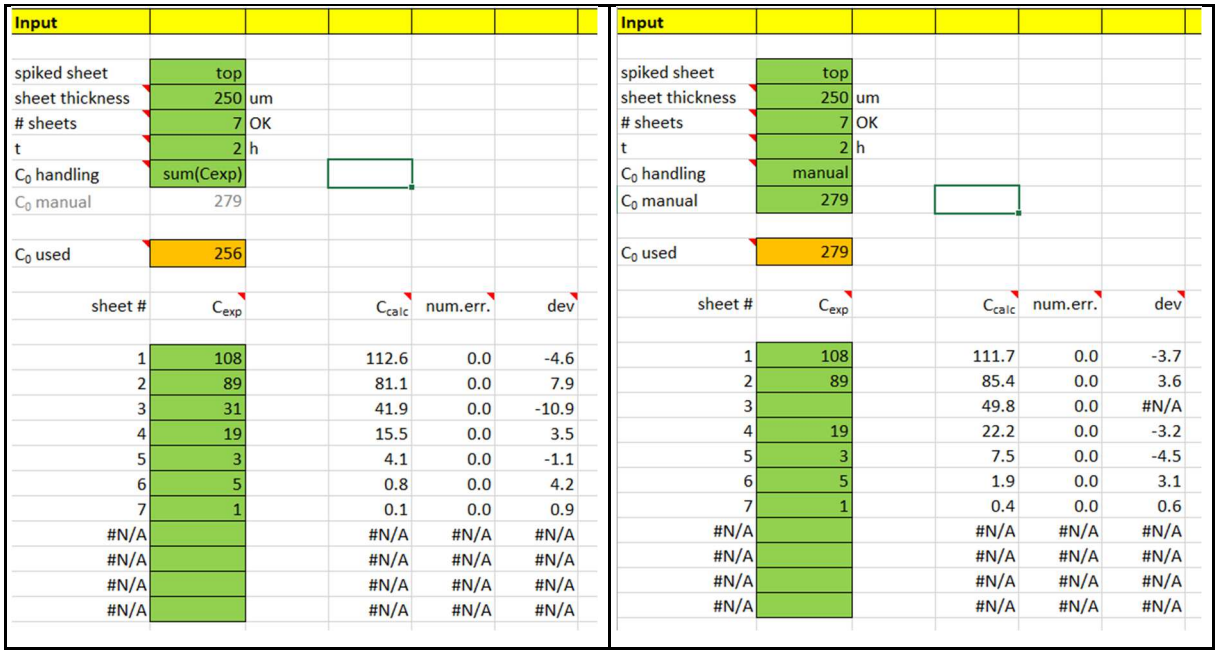
Save a read-only copy of the template as a backup, before making changes.

Top rows are hidden for convenience of the user. These rows are not locked or protected, and may be unhidden when required. Please read section 4 when you want to view hidden code.

Additional copies of the worksheet can be made within the workbook by CTRL-dragging the worksheet tab. When the plots do not appear in the copied worksheet, go to File, Options, Advanced, section "Cut, Copy, and Paste", and put a check mark at "Cut, copy, and sort inserted objects with their parent cells".

Specify Input data

Specify experimental conditions and concentration. Only edit the cells with green background.



Input					
spiked sheet	top				
sheet thickness	250	um			
# sheets	7	OK			
t	2	h			
C_0 handling	sum(Cexp)				
C_0 manual	279				
C_0 used	256				
sheet #	C_{exp}		C_{calc}	num.err.	dev
1	108		112.6	0.0	-4.6
2	89		81.1	0.0	7.9
3	31		41.9	0.0	-10.9
4	19		15.5	0.0	3.5
5	3		4.1	0.0	-1.1
6	5		0.8	0.0	4.2
7	1		0.1	0.0	0.9
#N/A			#N/A	#N/A	#N/A
#N/A			#N/A	#N/A	#N/A
#N/A			#N/A	#N/A	#N/A
#N/A			#N/A	#N/A	#N/A

Input					
spiked sheet	top				
sheet thickness	250	um			
# sheets	7	OK			
t	2	h			
C_0 handling	manual				
C_0 manual	279				
C_0 used	279				
sheet #	C_{exp}		C_{calc}	num.err.	dev
1	108		111.7	0.0	-3.7
2	89		85.4	0.0	3.6
3			49.8	0.0	#N/A
4	19		22.2	0.0	-3.2
5	3		7.5	0.0	-4.5
6	5		1.9	0.0	3.1
7	1		0.4	0.0	0.6
#N/A			#N/A	#N/A	#N/A
#N/A			#N/A	#N/A	#N/A
#N/A			#N/A	#N/A	#N/A
#N/A			#N/A	#N/A	#N/A

Spiked sheet = "top" or "center". Select from the drop-down list

Sheet thickness in micrometer

sheets = total number of sheets in the stack, including the spiked sheet

C_0 handling = "sum(Cexp)" or "manual". A basic assumption with the model is that the concentration in the spiked sheet at t = 0 is equal to the sum of all concentrations at time t. "Sum(Cexp)" is therefore generally best (leftmost screenshot above). The option "manual" can be chosen when concentrations in some sheets are not available due to sample loss. In this case an estimated C_0 must be used. For example, if the concentration in sheet #3 were missing, then an interpolated concentration of (89+19)/2=54 could be used. The manually specified value for C_0 could then be 279 (rightmost screenshot above).

"C_0 manual" is ignored and greyed out when "C_0 handling" = "sum(Cexp)"

"C_0 used" is given for information only. Do not change.

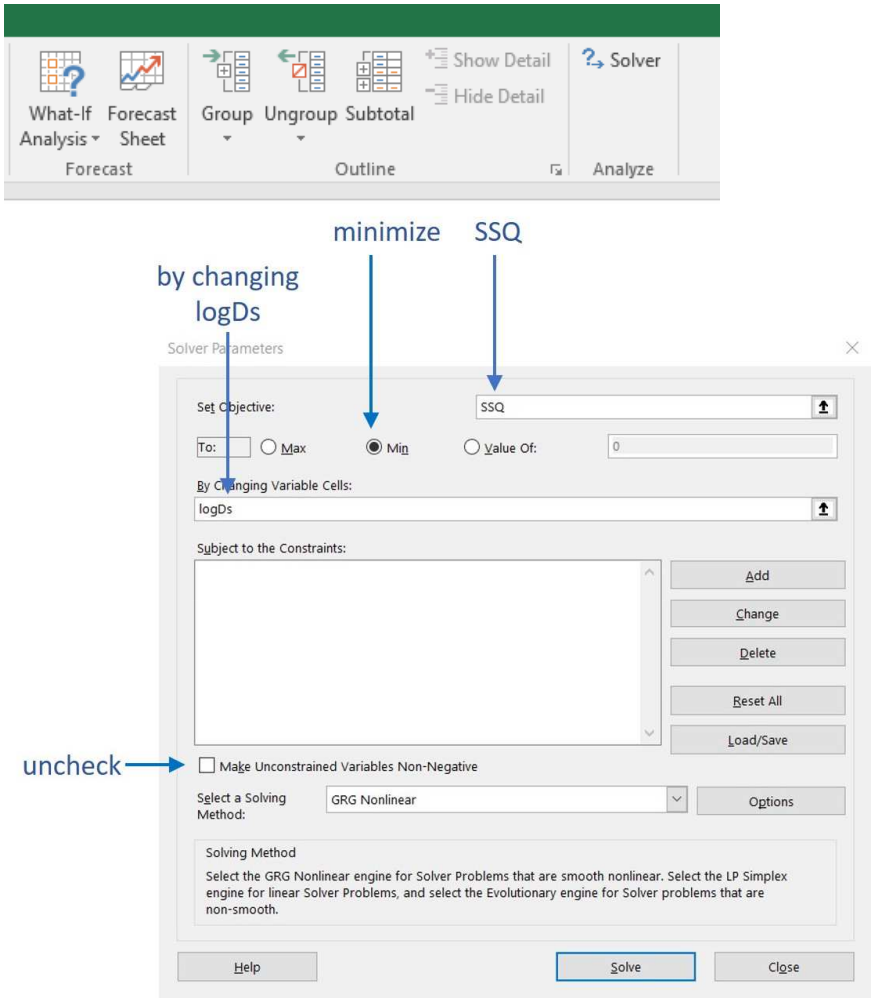
Experimental concentrations are specified in column C_{exp}. Concentrations in unused (#N/A) sheets must be left blank.

After parameter optimization column "C_{calc}" displays modelled concentrations. Column "num.err" lists truncation errors. Column "dev" shows the residual errors (experimental minus modeled concentrations).

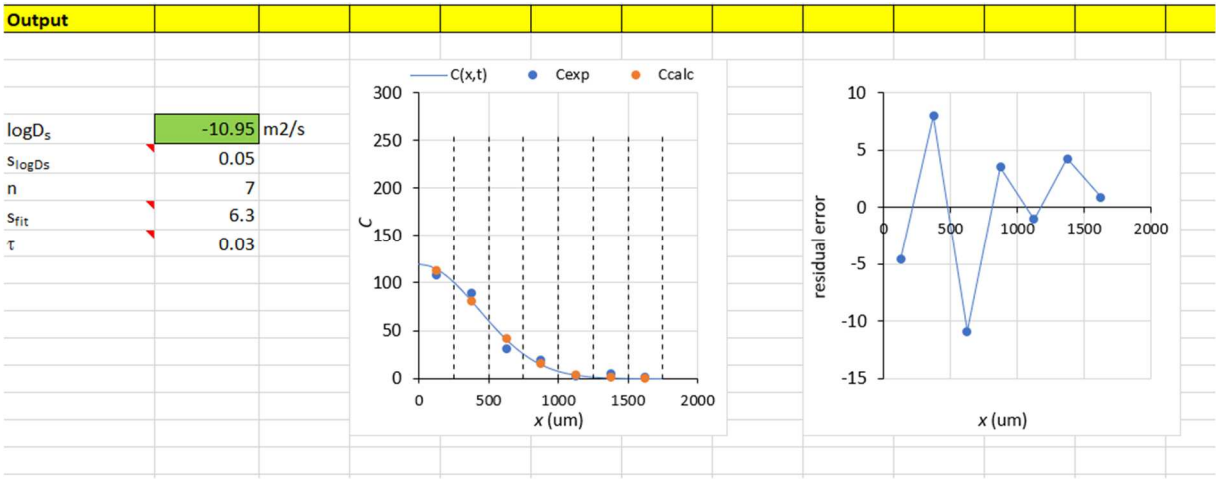
Run the model

Specify an initial value for logD_s in the cell with green background in section Output. This initial guess is not very critical, but avoid initial values that yield modeled concentrations that are the same for all sheets.

Then run Solver: Data tab, far right, click Solver. Check section 0 when Solver Add-in is not activated.



Solver returns with a message that it has found a solution or that it has converged to the current solution. Click OK and inspect the plots.



The leftmost plot shows concentrations versus distance. Blue circles are experimental values. Amber circles are modeled average concentrations within each sheet. The blue line shows modeled local concentrations. Hatched vertical lines represent sheet boundaries.

Rightmost plot shows residual errors (experimental minus modeled concentrations). Residual errors should be randomly distributed around zero. When modeled concentrations clearly do not match experimental concentrations, then run Solver again with a smaller (more negative) initial value of logD_s.

logD_s is the optimized estimate

s_{logDs} is the standard error in logD_s

n is the number of data points

s_{fit} is the standard error of the residuals

$\tau = D_s t/\ell^2$ is an indicator of equilibrium attainment. $\tau > 0.6$ indicates that concentrations in the sheets differ less than 0.5% from their equilibrium values, and $\tau > 0.3$ indicates that concentrations differ less than 10% from equilibrium.

3. Template validation

Present the template was tested against alternative models using fabricated data with nonzero noise. A comparison was made with the series model of cosines and exponentials (equation 4.56 from Crank, 1975). Differences in logD_s estimates were smaller than 10^{-5} log units (5 data sets for top-spiked stacks and 6 data sets for center-spiked stacks of 5 to 11 sheets). Differences in standard errors of logD_s were smaller than 10^{-7} log units.

Correctness of standard error estimates was verified by modeling 6 data sets for center-spiked sheets with the nls method from R-project (R Development Core Team, 2019). Differences in standard errors of logD_s were smaller than 10^{-5} log units.

Three data sets were modeled by numerical integration as outlined in Supplementary information 1 from Verhagen et al. (2019). Differences in logD_s estimates were smaller than 0.05 log units, and decreased to 0.03 log units when spatial resolution for the numerical integration method was increased from 10 to 20 data points per sheet. Experimental data from Verhagen et al. (2019) were extracted by digitizing their Figure 1, followed by estimation of logD_s using present template. Differences with listed values from these authors were smaller than 0.02 log units.

4. Code inspection

Code in the top rows can be inspected by unhiding these rows: select whole worksheet by clicking the triangle in the top left corner, followed by Home, Cells group, Format, Hide & Unhide, Unhide Rows. Take care to not accidentally convert array formulas to normal formulas. These cells have a light amber background. Array formulas are surrounded by curly braces {}. When you accidentally place cell content in edit mode by pressing F2 or clicking the formula bar, then leave edit mode by pressing ESC or CTRL+Shift+Enter.

5. Further support

Contact keesbooij@pasoc.eu when the template does not work as expected, or when you need additional features.

6. Terms of use

Template and associated manual are free to use. Multiple copies are allowed. The template may be modified as required, but may only be distributed further as is. Please cite this work as shown on the title page of this manual.

7. References

Belles, A., Franke, C., Alary, C., Aminot, Y., Readman, J.W., 2018. Understanding and predicting the diffusivity of organic compounds in polydimethylsiloxane material for passive sampler applications using a simple quantitative structure–property relationship model. Environmental Toxicology and Chemistry 37, 1291–1300. https://doi.org/10.1002/etc.4101

Billo, E.J., 2001. Non-linear regression using the solver., in: Excel for Chemists: A Comprehensive Guide. John Wiley & Sons, Inc., New York, pp. 223–238.

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R Development Core Team, 2019. R: A language and environment for statistical computing. Version 3.6.2. R Foundation for Statistical Computing, Vienna, Austria.

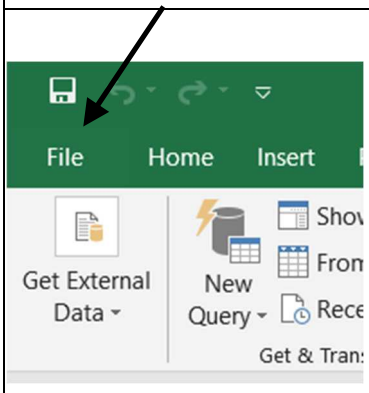
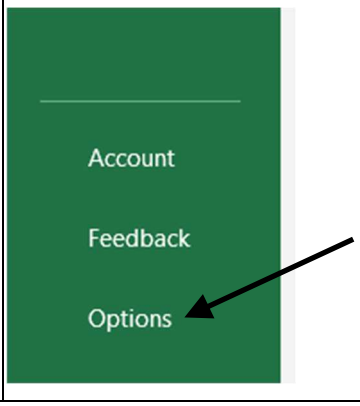
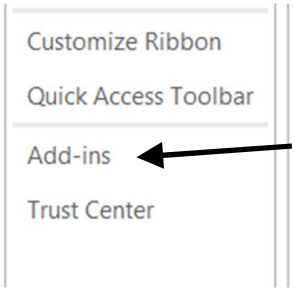
Rusina, T.P., Smedes, F., Klanova, J., 2010. Diffusion coefficients of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in polydimethylsiloxane and low-density polyethylene polymers. J.Appl.Polym.Sci. 116, 1803–1810. https://doi.org/10.1002/app.31704

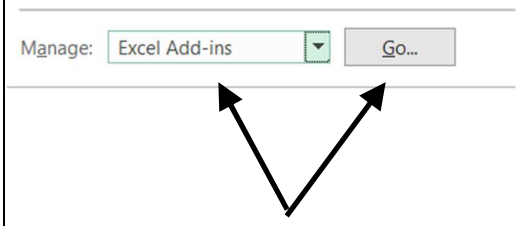
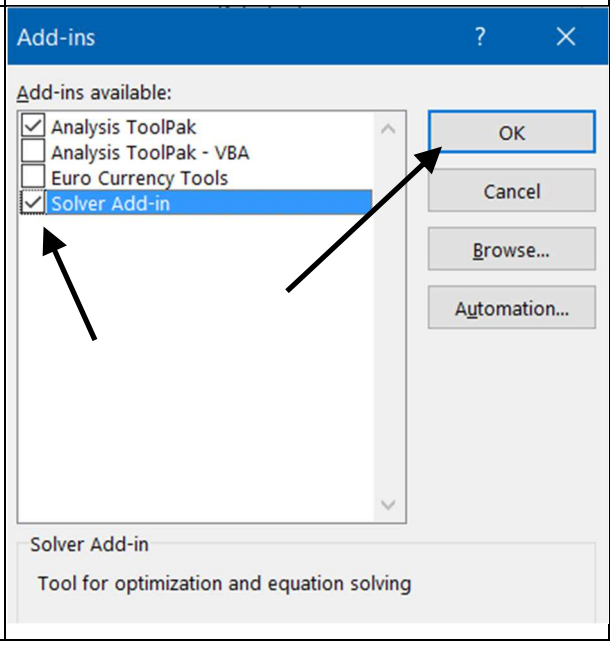
Verhagen, R., O'Malley, E., Smedes, F., Mueller, J.F., Kaserzon, S., 2019. Calibration parameters for the passive sampling of organic UV filters by silicone; diffusion coefficients and silicone–water partition coefficients. Chemosphere 223, 731–737. https://doi.org/10.1016/j.chemosphere.2019.02.077

Appendix: Activate Solver Add-in

If Solver Add-in is not activated:

- Go to https://support.microsoft.com/ and search "Load the solver add-in in Excel"
- or watch https://www.youtube.com/watch?v=W6tIS4JZ5J0
- or follow steps below

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.