

C_w calculation template for SSP-M823 passive samplers

Background information and manual

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Abstract

This document provides background information and instructions for use of an Excel template for calculating aqueous concentrations from deployed silicone passive sampler. The sampling rate model is based on water boundary layer controlled uptake rates. Silicone-water partition coefficients are obtained from experimental values. Justification for the use of these models is discussed.

1. Scientific background

Silicone passive samplers have been used for many years to monitor concentrations of freely dissolved nonpolar compounds in water. These concentrations (C_w) can be calculated from the accumulated amounts (N) by (Huckins et al., 2006; Smedes and Booij, 2012)

$$C_w = \frac{N}{m_p K_{pw} \left[1 - \exp\left(-\frac{R_s t}{m_p K_{pw}}\right) \right]} \quad 1$$

where t is time, R_s is (equivalent) water sampling rate, K_{pw} is polymer-water partition coefficient (volume per mass units) and m_s is polymer mass. When K_{pw} is given in volume per volume units, then the sampler volume (V_p) should be used instead of m_p . The accumulated amounts are determined by chemical analysis, and m_p is determined by weighing. Application of eq. 1 requires knowledge of R_s and K_{pw} , as discussed below.

Sampling rates

Sampling rates depend on flow and temperature. The performance reference compound (PRCs) method has been developed for the in-situ calibration of the uptake kinetics (Booij and Smedes, 2010; Huckins et al., 2002). PRCs are compounds of moderate hydrophobicity ($\log K_{ow}$ typically in the range 4 to 6) that do not occur in the environment, and are spiked into the samplers prior to deployment. The amounts of these compounds in the sampler (N) follow an exponential decrease with time

$$f = \frac{N}{N_0} = \exp\left(-\frac{R_s t}{m_p K_{pw}}\right) \quad 2$$

where N_0 is the amount present in the samplers at $t = 0$ (determined from analysis of unexposed samplers), f is the PRC fraction that is retained during the exposure. For sampling of nonpolar hydrophobic chemicals, the sampler-water exchange kinetics are generally controlled by transport through the water boundary layer (WBL). In this case, R_s is proportional to the diffusion coefficient in water (D_w) to the power 2/3 (Booij et al., 2003; Booij and Smedes, 2010). Schwarzenbach et al. (2003) showed that molecular weight can be used as a predictor of D_w at 25 °C

$$D_w = \frac{2.7 \times 10^{-8}}{MW^{0.71}} \quad 3$$

where D_w is given in m^2/s . Hence, the R_s for WBL controlled kinetics is inversely proportional to the molecular weight to the power $0.71 \times 2/3 = 0.47$

$$R_s = \frac{\beta_M}{MW^{0.47}} \quad 4$$

where β_M reflects the exposure-specific effect on R_s , and MW takes the compound-specific effect on R_s into account. Putting everything together, PRC dissipation can be modelled by

$$f = \frac{N}{N_0} = \exp\left(-\frac{\beta_M t}{m_p K_{pw} MW^{0.47}}\right) \quad 5$$

β_M is obtained by nonlinear least squares estimation of f as a function of $K_{pw} M^{0.47}$. Aqueous concentrations of the target chemicals can be calculated from

$$C_w = \frac{N}{m_p K_{pw} \left[1 - \exp\left(-\frac{\beta_M t}{m_p K_{pw} MW^{0.47}}\right) \right]} \quad 6$$

WBL controlled exchange kinetics can be assumed when

$$\frac{R_s L}{AD_p K_{pw} \rho} \ll 3 \quad 7$$

where A is surface area of the sampler ($2 \times \text{length} \times \text{width}$), L is half-thickness, ρ density, and D_p is diffusion coefficient in the polymer. With silicone samplers the left hand side of eq. 7 is typically (much) smaller than 0.01 for nonpolar compounds (PCBs, PBDEs, PAHs, pyrethroids) and slightly polar compounds (DDTs, HCHs, drins). Silicone samplers are not so useful for sampling of very polar compounds because these analytes have small K_{pw} values (<100) and quickly reach sampler-water equilibrium, which challenges the samplers' ability to yield time-integrated aqueous concentrations.

Silicone-water partition coefficients

Experimental K_{pw} values are preferred over values that are based on correlations with $\log K_{ow}$ or linear free energy relationships (LFERs). Experimental K_{pw} values for SSP-M823 been obtained for a variety of nonpolar and polar compounds (Grant et al., 2016; Kwon et al., 2007; Smedes, 2019). These values are included in the template for convenience of the user. Accuracy of K_{pw} is only critical for chemicals that attain partial or complete equilibrium during the exposure, i.e. for PRCs and for chemicals with $\log K_{pw}$ values < 6. The more hydrophobic compounds generally reach an insignificant degree of equilibrium during typical exposure periods of 3 to 6 weeks, and uncertainties in their K_{pw} values have a negligible effect on the accuracy of the measured aqueous concentrations.

When experimental values are not available, PaSOC is happy to estimate K_{pw} from K_{ow} and/or LFERs, if needed.

Temperature and salinity effects on K_{pw}

Lower temperatures and higher salinities result in higher K_{pw} . A temperature decrease by 10 °C causes K_{pw} to increase by a factor of 1.15 to 2.5, and this increase is generally larger for the more hydrophobic compounds (Jonker et al., 2015; Lohmann, 2012). K_{pw} values in seawater can be a factor of 1.5 larger in seawater as compared with freshwater (Jonker et al., 2015).

Present template deliberately does not account for temperature and salinity effects on K_{pw} for several reasons. First, ignoring the effects of lower temperatures causes an overestimation of C_w . However, bioaccumulation factors of nonpolar compounds are also larger at lower temperature (Muijs and Jonker, 2009). This means that the overestimated C_w still gives a fair prediction of bioaccumulation potential when bioaccumulation factors at 20 °C are used (Ghosh et al., 2014, Supplemental data, page 4). Second, the parameters that are needed to make temperature and salinity corrections are not abundant, and not readily available for many compounds of interest. Third, overestimation of C_w at lower temperature and higher salinity is relatively independent of location and compound hydrophobicity (Jonker et al., 2015, Figures S6 and S7A). Bottom line of these considerations is that neglecting the effects of temperature and salinity does not greatly affect the accuracy of passive sampling based monitoring, although PaSOC is happy to adapt the template to account for temperature and salinity effects if needed.

2. Use of the C_w calculation template

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

Properties worksheet

The “Properties” worksheet contains compound names, CAS numbers, and values for molecular weight, $\log K_{ow}$, and $\log K_{pw}$ data from three literature sources. These values are supplied for the consideration of the user. Column E contains the $\log K_{pw}$ values that are used in the calculations, which may be replaced with other values as required.

compound group	compound	CAS	MW	$\log K_{pw}$	source $\log K_{pw}$
Additional rows can be inserted between the highlighted rows, if needed. Do not insert or delete columns. Do not delete the highlighted rows.					
PCBs	PCB 1	2051-60-7	188.7	4.04	Smedes 2019
PCBs	PCB 2	2051-61-8	188.7	4.18	Smedes 2019
PCBs	PCB 3	2051-62-9	188.7	4.15	Smedes 2019
PCBs	PCB 4	13029-08-8	223.1	4.20	Smedes 2019
PCBs	PCB 10	33146-45-1	223.1	4.35	Smedes 2019
PCBs	PCB 14	34883-41-5	223.1	4.81	Smedes 2019
PCBs	PCB 18	37680-65-2	257.5	4.95	Smedes 2019
PCBs	PCB 21	55702-46-0	257.5	5.14	Smedes 2019
PCBs	PCB 28	7012-37-5	257.5	5.25	Smedes 2019
PCBs	PCB 29	15862-07-4	257.5	5.19	Smedes 2019
PCBs	PCB 30	25602-07-6	257.5	5.01	Smedes 2019

Compound names may be changed according to user preference.

Cells in column A-F, between the highlighted rows are part of a VLOOKUP range that is used to retrieve data for the C_w calculation in worksheet “Cw”. Rows may be deleted, moved, copied, or inserted as required, but do not delete the highlighted rows.

Columns A-F should not be deleted, inserted, or moved, since this invalidates the column references in the VLOOKUP function.

C_w worksheet

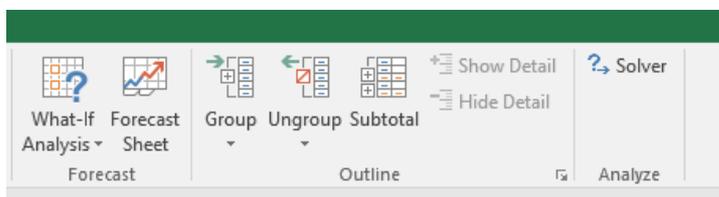
Rows 1-116 are hidden for convenience of the user. These rows are not locked or protected, and may be unhidden when required.

Columns A-Z are used for input data (PRC fractions and amounts of target compounds). Model output is shown in columns AB-AX

Cells with a green background should be filled out by the user. The other cells should not be changed.

A maximum of 20 exposures can be processed together.

Check that the solver add-in is activated (Data tab, far right, should display the word “Solver”)



Block 1 : Method information

This part contains a summary of the model and the source of the K_{pw} data.

Block 1				
R_s model				
model eq.				$R_s = \beta_M / MW^{0.47}$
model ref.				Rusina et al. ES&T 44: 362–367, 2010
adjustable parameter	$L d^{-1} g^{0.47} mol^{-0.47}$			β_M
K_{pw} data				
				retrieve from worksheet "properties"

Block 2: Exposure data

Block 2				
Exposure data				
Exposure ID			site1	site2
exposure time		d	27	27
sampler mass		kg	0.0034	0.0035
sampler surface area		dm ²	0.99	0.99

Exposure ID: Any name

Exposure time in days.

Sampler mass in kg.

Sampler surface area: exchange surface area ($2 \times \text{length} \times \text{width}$). This is used to calculate surface area normalised sampling rates.

Block 3: PRC data

Twenty rows with PRC data can be used in the calculations.

Keep the number of rows at 20; do not insert or delete rows from this block. Do not sort or move rows within this block.

Rows that are left blank are ignored.

Block 3				
Retained PRC fractions				
PRC name	MW	$\log K_{pw}$	f_{obs}	f_{obs}
fluorene-D10	176.20	3.44	0.000	0.000
anthracene-D10	188.20	3.88	0.000	0.000
pyrene-d10	212.25	4.34	0.031	0.032
chrysene-d12	240.36	4.80	0.320	0.311
PCB 10	223.10	4.35	0.036	0.034
PCB 30	257.54	5.01	0.506	0.520
PCB 104	326.43	5.88	0.921	0.809
PCB 145	360.88	6.44	0.979	1.007
PCB 204	429.77	7.43	0.998	1.019
PCB 170	not used	not used		
PCB 180	not used	not used		
PCB 187	not used	not used		
PCB 189	not used	not used		
PCB 204	not used	not used		
PCB 182	not used	not used		
PCB 206	not used	not used		
PCB 209	not used	not used		

Specify the name of the PRCs in the first column by selecting compound name from the drop-down list. Changes in compound names and list order should be made in the worksheet "Properties".

Compounds may be added to, or removed from to the list, by inserting/deleting rows in the worksheet "Properties". (See above.)

Values for $\log K_{pw}$ and MW are retrieved from worksheet "Properties", using a VLOOKUP function.

"not used" appears when PRC name is left blank.

Type retained PRC fractions in the columns with header " f_{obs} ", or fill in from another worksheet using copy + paste values. Blank cells are ignored in the calculations.

Block 4: Accumulated amounts

Block 4				
Accumulated amounts				
compound	MW	$\log K_{pw,0}$	N (ng)	N (ng)
phenanthrene	178.23	3.82	35.5	70.6
fluoranthene	202.25	4.28	672.4	441.9
pyrene	202.25	4.39	14.5	14.6
benzo[a]pyrene	252.31	5.26	8.3	16.6
PCB 28	257.54	5.25	1.5	1.5
PCB 52	291.99	5.52	4.9	3.8
PCB 101	326.43	5.99	6.3	14.7
PCB 118	326.43	6.11	49.2	3.9
PCB 153	360.88	6.45	409.7	459.0
PCB 138	360.88	6.49	287.5	110.7
PCB 180	395.32	6.76	162.0	79.9
4,4'-DDE	318.03	6.04	70.8	35.6

Select compound names of target analytes from the drop-down list.

Number of rows can be reduced by deleting rows, or increased by copy/pasting rows from the bottom downwards. Always keep the top row.

Block 5: Results

Run the solver add-in before inspecting the results (Far right on Data tab, Solver, Solve, OK). When Solver reports a convergence error, try an initial default value of $\beta_M = 100$ in block 5.

Solver Parameters

Set Objective:

To: Max Min Value Of:

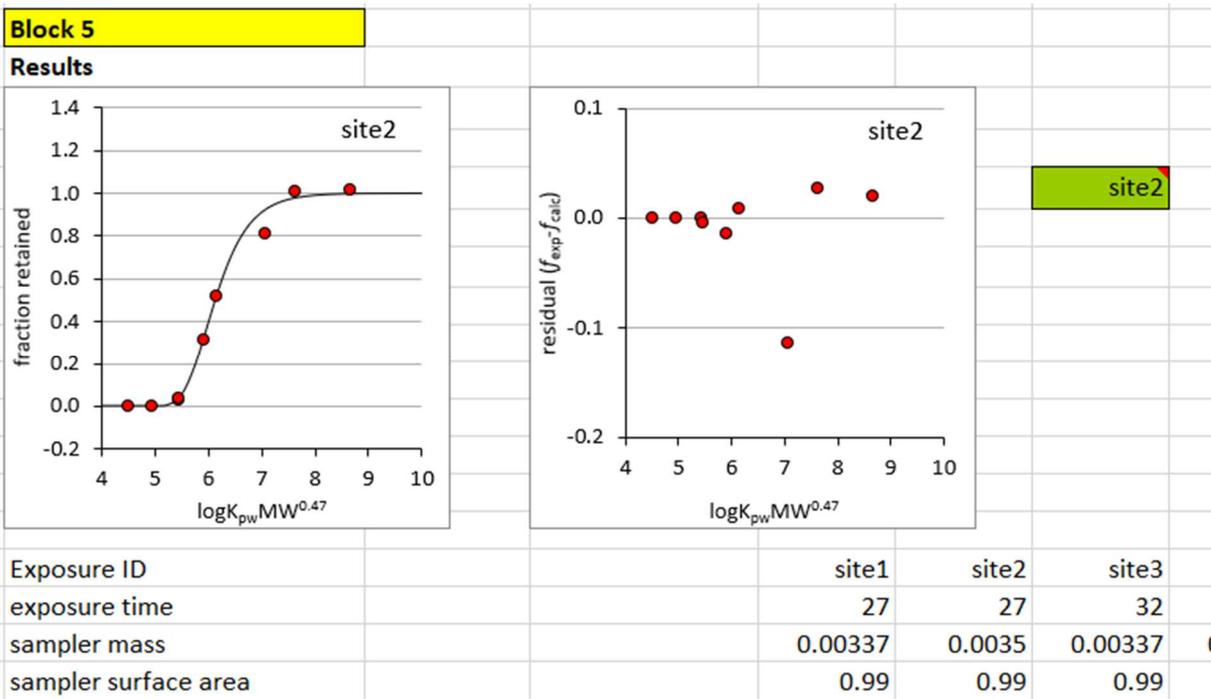
By Changing Variable Cells:

Subject to the Constraints:

Make Unconstrained Variables Non-Negative

Select a Solving Method:

Solving Method
Select the GRG Nonlinear engine for Solver Problems that are smooth nonlinear. Select the LP Simplex engine for linear Solver Problems, and select the Evolutionary engine for Solver problems that are non-smooth.



At the top of the Results block inspect how well the model fits the retained PRC fractions.

Select the exposure of interest from the drop down box of the green cell.

Left plot shows retained PRC fractions and model fit. Right plot shows residual errors (difference between experimental and modelled fractions).

Vertical and horizontal scales can be modified as required.

Numerical results of the least squares estimation is shown below the graphs.

Model output		site1	site2
estimated β_M	$L d^{-1} g^{0.47} mol^{-0.47}$	118.1	120.9
S.E. in β_M	$L d^{-1} g^{0.47} mol^{-0.47}$	0.0	9.6
$R_{s\ 300}$	L/d	8.1	8.3
S.E. in R_s	L/d	0.0	0.7
n		9	9
s_{fit}	-	0.00	0.04
$R_{s\ 300} * t$	L	219	224
$R_{s\ 300}/A$	$L dm^{-2} d^{-1}$	8.2	8.4
smallest $f_{exp} - f_{calc}$	-	0.00	-0.11
largest $f_{exp} - f_{calc}$	-	0.00	0.03

Estimated β_M and its standard error (S.E.) are shown in the first two rows. These values are used in the C_w calculations, but are difficult to interpret. Therefore estimated R_s of a reference compound with $MW = 300 g mol^{-1}$ and associated standard error are listed for reference.

n is the number of PRC data that were used

s_{fit} is the standard error of the model fit.

$R_{s,300} * t$ gives an indication of the equivalent water volume that is extracted for compounds that remained in the kinetic sampling stage.

$R_{s,300}/A$ gives an indication of the mass transfer coefficient of the water boundary layer. This value typically is in the range $1 L dm^{-2} d^{-1}$ for quiescent waters and $50 L dm^{-2} d^{-1}$ for very turbulent waters (flow velocities of several $m s^{-1}$).

Smallest and largest residual errors are listed to help find the range that should be used for the residuals plot.

Block 6: C_w summary

Aqueous concentrations, exposure parameters, and model parameters are summarized in the rows below the model output.

Block 6				
Aqueous concentrations				
compound	MW	$\log K_{pw}$	C_w (pg/L)	C_w (pg/L)
phenanthrene	178.23	3.82	1592.6	3053.6
fluoranthene	202.25	4.28	10648.0	6745.5
pyrene	202.25	4.39	182.4	177.9
benzo[a]pyrene	252.31	5.26	42.1	82.4
PCB 28	257.54	5.25	8.0	7.5
PCB 52	291.99	5.52	24.6	18.7
PCB 101	326.43	5.99	30.8	70.6
PCB 118	326.43	6.11	240.1	18.6
PCB 153	360.88	6.45	2066.6	2261.7
PCB 138	360.88	6.49	1448.9	545.2
PCB 180	395.32	6.76	848.3	408.9
4,4'-DDE	318.03	6.04	342.6	168.3

The output data from blocks 5 and 6 can be copied and pasted as values in another workbook, for reporting and further processing.

Note on replication

Sampler replicates can be processed based on the PRC and accumulated amount data for the individual samplers, but it is often better to apply a different pooling strategy. Absorbed amounts for replicates within the same exposure are usually highly similar, which indicates that the actual sampling rates are also similar. PRC based R_s estimates are usually more variable than accumulated amounts. This suggests that PRC data are preferably pooled, prior to the calculation of C_w for the individual samplers, as shown on next page.

3. Template validation

The template was tested using fabricated sampler data with zero noise (random exposure time, sampler thickness, area, sampling rate). Ratios of model output (β_M , $R_{s,300}$, C_w) and imposed data were 1.00000 ± 0.00001 .

Uncertainty estimates from the template were tested using fabricated sampler data with 5% random noise on the retained fractions. Estimates of β_M and its standard error were determined using present template and the nls method from R-project (R Development Core Team, 2019). Ratios of β_M and its standard error were 1.00000 ± 0.00001 .

Block 2					
Exposure data					
Exposure ID				Replicate1	Replicate2
exposure time		d	PRC data for	27	27
sampler mass		kg	Replicate 1	0.0034	0.0034
sampler surface area		dm ²		0.99	0.99
Block 3					
Retained PRC fractions					
PRC name	MW	logK _{pw}		f _{obs}	f _{obs}
fluorene-D10	176.20	3.44		0.000	0.000
anthracene-D10	188.20	3.88		0.000	0.000
pyrene-d10	212.25	4.34		0.031	0.031
chrysene-d12	240.36	4.80		0.284	0.284
PCB 10	223.10	4.35		0.037	0.037
PCB 30	257.54	5.01		0.504	0.504
PCB 104	326.43	5.88		0.910	0.910
PCB 145	360.88	6.44		0.977	0.977
PCB 204	429.77	7.43		0.957	0.957
fluorene-D10	176.20	3.44		0.000	0.000
anthracene-D10	188.20	3.88		0.000	0.000
pyrene-d10	212.25	4.34		0.030	0.030
chrysene-d12	240.36	4.80		0.323	0.323
PCB 10	223.10	4.35		0.037	0.037
PCB 30	257.54	5.01		0.558	0.558
PCB 104	326.43	5.88		0.999	0.999
PCB 145	360.88	6.44		1.004	1.004
PCB 204	429.77	7.43		0.912	0.912
	not used	not used			
	not used	not used			

PRC data for Replicate 1

PRC data for Replicate 2

4. Further support

This template comes with free online instructions for each purchase. Approximately 30 min should be sufficient. Contact keesbooi@pasoc.eu to set a date and time for this.

Contact keesbooi@pasoc.eu when the template needs to be tailored to your specific needs, when you need additional K_{pw} estimates, or when the template does not work as expected.

5. Terms of use

Terms of use are summarised on the Readme tab of the template.

6. References

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