

# **$C_w$ calculation with contaminant mass ratio approach**

## **Background information and manual**

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## Abstract

This document provides background information and instructions for use of the Excel template for calculating aqueous concentrations from co-deployed passive samplers of different thickness. In-situ calibration of the kinetics is done by modelling the ratio of accumulated amounts in these samplers. This method can be used for sampling of nonpolar compounds by single-phase polymers when uptake kinetics is controlled by the water boundary layer.

## 1. Scientific background

Single -phase polymers (e.g., silicone, low-density polyethylene – LDPE) have been used for many years to monitor concentrations of freely dissolved nonpolar compounds in water. Aqueous concentrations ( $C_w$ ) can be calculated from the accumulated amounts ( $N$ ) by (Huckins et al., 2006; Smedes and Booij, 2012)

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

where  $t$  is time,  $R_s$  is (equivalent) water sampling rate,  $K_{sw}$  is sorbent-water partition coefficient (volume per mass units) and  $m_s$  is sorbent mass. When  $K_{sw}$  is given in volume per volume units, then the sampler volume ( $V_s$ ) should be used instead of  $m_s$ . Sorption coefficients are determined experimentally, or are obtained from correlations with compound properties (e.g.,  $\log K_{ow}$ ). Sampling rates  $R_s$  depend on water flow velocities, and are weakly dependent on molecular size because diffusion coefficients in water ( $D_w$ ) decrease with molecular size. For example,  $D_w$  of phenanthrene is approximately two times larger than the  $D_w$  of BDE153.

The most frequently used method for in-situ calibration of  $R_s$  is to model the dissipation of performance reference compounds (PRCs), which are spiked into the sorbent prior to exposure. PRCs with high  $K_{sw}$  are almost completely retained during the exposure, and PRCs with low  $K_{sw}$  are almost completely dissipated.

The contaminant mass ratio (CMR) method allows for in-situ calibration without PRCs. With this method, two samplers with different thickness and same surface area are deployed together (Fuchte et al., 2020). Compounds with low  $K_{sw}$  attain sampler-water equilibrium, and their amount ratios between thin and thick samplers are equal to the sampler mass ratios. Amounts of compounds with high  $K_{sw}$  are the same in thin and thick sampler (ratio = 1) because accumulation is not limited by equilibrium attainment.

Before going into details on the CMR model, some assumptions regarding the dependency of  $R_s$  on molecular size are discussed.

### Molecular size dependency of $R_s$

For sampling of nonpolar chemicals by silicone and LDPE, the sampler-water exchange kinetics are 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; Levich, 1962; Opdyke et al., 1987).

Experimental values of  $D_w$  of nonpolar compounds are rather scarce, and are more conveniently obtained from correlations with molecular size. Schwarzenbach et al. (2003) showed that molecular weight can be used as a predictor of  $D_w$  at 25 °C

$$D_w \text{ (in m}^2\text{/s)} = \frac{2.7 \times 10^{-8}}{MW^{0.71}} \quad 2$$

This equation was later updated by these authors (Schwarzenbach et al., 2016) to

$$D_w \text{ (in m}^2\text{/s)} = \frac{7.0 \times 10^{-9}}{MW^{0.45}} \quad 3$$

A slightly better correlation was found by Schwarzenbach et al. (2016) between  $D_w$  and McGowan molar volume ( $V_{McG}$ ) (Abraham and McGowan, 1987)

$$D_w \text{ (in m}^2\text{/s)} = \frac{1.52 \times 10^{-8}}{V_{McG}^{0.45}} \quad 4$$

Present mainstream modelling of  $R_s$  is based on equation 2, which is therefore adopted in present  $C_w$  calculation template.

$$R_s = \frac{\beta_M}{MW^{0.47}} \quad 5$$

where  $\beta_M$  is a proportionality constant and the power of  $MW$  originates from  $0.71 \times 2/3 = 0.47$ . This constant is difficult to interpret, and it is therefore useful to report the sampling rate of a reference compound with  $MW = 300$  (that is  $R_{s,300} = \beta_M / 300^{0.47}$ ). The present  $C_w$  calculation template can be adapted if users prefer equations 3 or 4 over equation 2.

### CMR method

Combining equations 1 and 5 gives an expression of the amount ratio in samplers with different thickness

$$\frac{N_1}{N_2} = \frac{m_1 \left[ 1 - \exp\left(-\frac{\beta_M t}{m_1 K_{sw} MW^{0.47}}\right) \right]}{m_2 \left[ 1 - \exp\left(-\frac{\beta_M t}{m_2 K_{sw} MW^{0.47}}\right) \right]} \quad 6$$

An example of the CMR model approach is shown in Figure 1 for PCB and PAH sampling with 0.25 and 0.50 mm thick silicone samplers that have the same surface area. Compounds with low  $\log K_{sw}$  attain equilibrium in both samplers, and the amount ratios are therefore equal to the sampler mass ratio ( $m_1/m_2 = 0.5$ , in this case). Compounds with high  $\log K_{sw}$  remain in the kinetic sampling stage, and their amount ratios are therefore equal to 1. At higher flow the curve in Figure 1 shifts to the right (higher degree of equilibrium for both samplers).

The  $C_w$  calculation template yields a best estimate of  $\beta_M$ , which can be used to calculate  $C_w$  from

$$C_w = \frac{N_1}{m_1 K_{sw} \left[ 1 - \exp\left(-\frac{\beta_M t}{m_1 K_{sw} MW^{0.47}}\right) \right]} \quad 7$$

and a second  $C_w$  estimate can be obtained similarly from  $N_2$ . These calculations are done automatically by the template. The standard error in  $\beta_M$ , and  $R_{s,300}$  with associated standard errors are also automatically calculated.

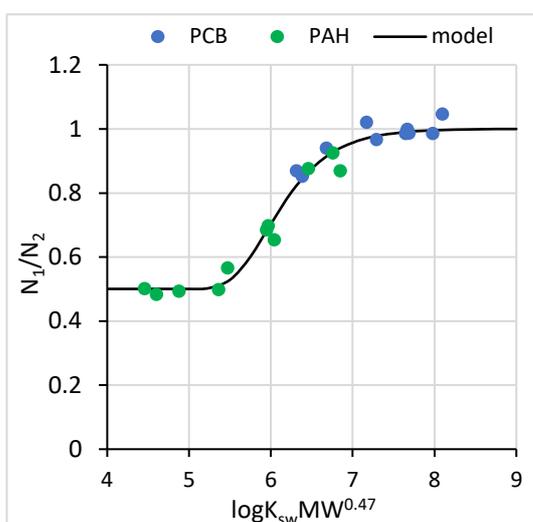


Figure 1. Amount ratios of PCBs (blue) and PAHs (green) in 0.25 mm and 0.50 mm silicone sampler with exchange surface area  $1.0 \text{ dm}^2$  that are exposed for 28 d at a flow that results in  $R_{s,300} = 6.4 \text{ L/d}$ . Equation 6 is shown as a solid line.

### **Sampler-water partition coefficients**

The template includes a set of experimental  $\log K_{sw}$  values for SSP-M823 silicone, but these can be replaced by values for other silicones or for LDPE. The  $\log K_{sw}$  list can be edited (replace values, add or delete compounds) according to user preference, without affecting the model calculation scheme.

### **Temperature and salinity effects on $K_{sw}$**

Lower temperatures and higher salinities result in higher  $K_{sw}$ . A temperature decrease by 10 °C causes  $K_{sw}$  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).  $K_{sw}$  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  $K_{sw}$  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 (Figures S6 and S7A from Jonker et al., 2015). 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

Worksheet "Properties" contains compound names, CAS numbers, and values for molecular weight,  $\log K_{ow}$ , and  $\log K_{sw}$  data from literature sources. These values are supplied for the consideration of the user. Column E contains the  $\log K_{sw}$  values that are used in the calculations. These may be replaced by other values as required.

compound group	compound	CAS	MW	$\log K_{sw}$	source $\log K_{sw}$
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

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, 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

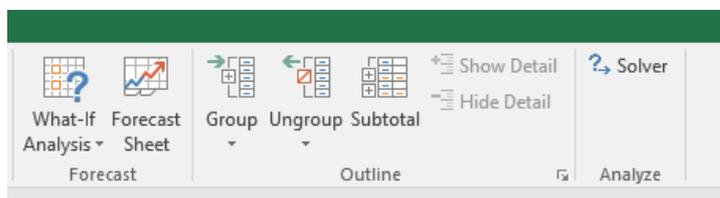
Rows 1-200 are hidden for convenience of the user. These rows are not locked or protected, and may be unhidden when required.

Columns A-W are used for input data (accumulated amounts in thin and thick samplers). Model output is shown in columns AA-AW

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

A maximum of 10 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  $K_{sw}$  data.

Block 1				
<b>R<sub>s</sub> model</b>				
model eq.			$R_s = \beta_M / MW^{0.47}$	
model ref.			Rusina et al. ES&T 44: 362–367, 2010	
adjustable parameter	$L d^{-1} g^{0.47} mol^{-0.47}$		$\beta_M$	
<b>K<sub>sw</sub> data</b>				
			retrieve from worksheet "properties"	

**Block 2: Exposure data**

Block 2				
<b>Exposure data</b>				
Exposure ID			site1	
exposure time		d	28	
sampler mass		kg	0.0015	0.0029
sampler surface area		dm <sup>2</sup>	1.00	

Exposure ID: Any name

Exposure time in days.

Sampler mass of thin and thick samplers 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.

Exposure data can be entered manually, or by using copy/paste, or by linking to another worksheet or workbook.

**Block 3: Amount data**

Thirty compounds can be processed. PaSOC will extend this number for free, if needed.

Select compound names from the drop down boxes in column A. Do not insert, delete, move, or sort rows or columns.

Rows that are left blank are ignored. Missing amount data are allowed.

Block 3				
Amount data				
compound	MW	logK <sub>sw</sub>	N <sub>1</sub> (ng)	N <sub>2</sub> (ng)
PCB 28	257.54	5.25	77.0	90.3
PCB 31	257.54	5.18	9.5	10.9
PCB 52	291.99	5.52	38.4	40.9
PCB 101	326.43	5.99	472.9	463.3
PCB 118	326.43	6.11	114.3	118.1
PCB 138	360.88	6.49	697.0	706.2
PCB 153	360.88	6.45	27.7	28.1
PCB 156	360.88	6.47	6.3	6.3
PCB 156	395.32	6.88	21.4	20.4
PCB 157	395.32	6.76	28.9	29.4
PCB 167	154.21	3.43	6.0	12.0
PCB 169	166.22	3.56	13.1	27.1
PCB 170	178.23	3.82	58.5	118.8
PCB 180	202.25	4.28	280.6	563.2
PCB 182	202.25	4.39	704.1	1243.8
PCB 187	228.29	4.86	1170.4	1678.6
Pyrene	202.25	4.39	704.1	1243.8
Benzo[a]anthracene	228.29	4.86	1170.4	1678.6

Changes in compound names and order of compound names in the drop down box should be made in the worksheet “Properties”. Compounds may be added to, or removed from the list, by inserting/deleting/moving rows in the worksheet “Properties”. (See section Properties worksheet above.)

Values for logK<sub>sw</sub> and MW are retrieved from worksheet “Properties”, using a VLOOKUP function. “not used” appears when compound name is left blank.

Type amounts columns in the columns with header “N<sub>1</sub>” and “N<sub>2</sub>”, or copy/paste from another worksheet, or link to another worksheet or workbook. Blank cells are ignored in the calculations.

#### Block 4: 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 4.

Solver Parameters

Set Objective:

To:  Max  Min  Value Of:

By Changing Variable Cells:

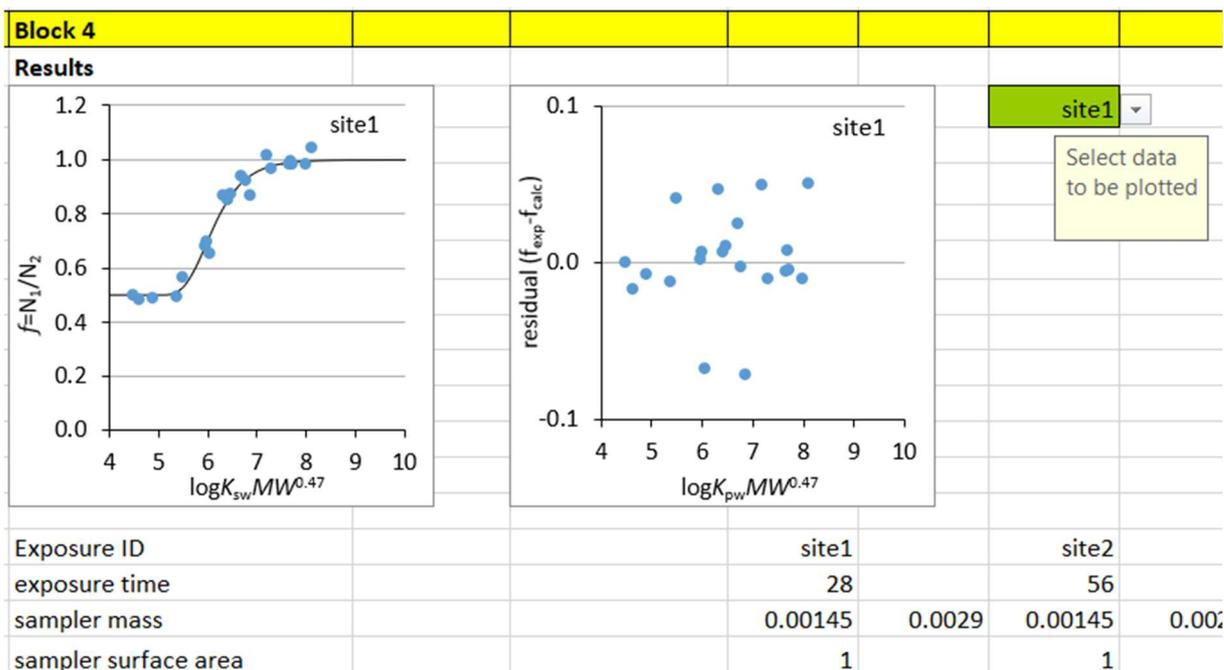
Subject to the Constraints:

Make Unconstrained Variables Non-Negative

Select a Solving Method:  Options

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.

Help Solve Close



At the top of the block 4 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 amount ratios and model fit. Right plot shows residual errors (difference between experimental and modelled fractions).

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

Model output		site1	site2
estimated $\beta_M$	$\text{L d}^{-1} \text{g}^{0.47} \text{mol}^{-0.47}$	93.0	192.0
S.E. in $\beta_M$	$\text{L d}^{-1} \text{g}^{0.47} \text{mol}^{-0.47}$	7.1	20.6
$R_{s\ 300}$	L/d	6.4	13.2
S.E. in $R_s$	L/d	0.5	1.4
n		21	21
$s_{\text{fit}}$	-	0.03	0.05
$R_{s\ 300} * t$	L	178	737
$R_{s\ 300}/A$	$\text{L dm}^{-2} \text{d}^{-1}$	6.4	13.2
smallest $f_{\text{exp}} - f_{\text{calc}}$	-	-0.07	-0.08
largest $f_{\text{exp}} - f_{\text{calc}}$	-	0.05	0.10

Estimated  $\beta_M$  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  $MW = 300 \text{ g mol}^{-1}$  and associated standard error are listed for reference.

$n$  is the number of amount ratios that were used

$s_{\text{fit}}$  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  $1 \text{ L dm}^{-2} \text{d}^{-1}$  for quiescent waters and  $50 \text{ L dm}^{-2} \text{d}^{-1}$  for very turbulent waters (flow velocities of several  $\text{m s}^{-1}$ ).

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

## Block 5: $C_w$ summary

Aqueous concentrations are listed in block 5.

Block 5					
Aqueous concentrations					
compound	MW	$\log K_{sw}$	$C_w$ (pg/L)	$C_w$ (pg/L)	$C_w$ (pg/L)
PCB 28	257.54	5.25	569.4	564.5	564.5
PCB 31	257.54	5.18	74.3	70.3	70.3
PCB 52	291.99	5.52	255.3	248.4	248.4
PCB 101	326.43	5.99	2929.2	2785.4	2785.4
PCB 118	326.43	6.11	697.7	705.2	705.2
PCB 138	360.88	6.49	4340.9	4358.4	4358.4
PCB 153	360.88	6.45	172.6	173.4	173.4
PCB 156	360.88	6.47	39.0	38.7	38.7
PCB 170	395.32	6.88	137.6	131.0	131.0
PCB 180	395.32	6.76	186.5	188.4	188.4
Acenaphthene	154.21	3.43	1544.9	1542.2	1542.2
Fluorene	166.22	3.56	2487.9	2572.9	2572.9
Phenanthrene	178.23	3.82	6111.2	6198.4	6198.4
Fluoranthene	202.25	4.28	10161.8	10406.0	10406.0
Pyrene	202.25	4.39	19830.5	18372.8	18372.8

The output data from blocks 4 and 5 can be copied and pasted as values in another workbook, for reporting and further processing.

### 3. Template validation

The template was tested using ten sets of fabricated sampler data with zero noise (random exposure time, sampler thickness, area, sampling rate). Model output ( $\beta_M$ ,  $R_{s,300}$ ,  $C_w$ ) agreed within 0.0001% relative to the imposed values.

Uncertainty estimates from the template were tested using ten sets of fabricated sampler data with 1 to 8% random noise on the amounts. Estimates of  $\beta_M$  and its standard error were determined using present template and the nls method from R-project (R Development Core Team, 2019). Estimates of  $\beta_M$  and its standard error agreed within 0.001%.

### 4. Further support

This template comes with free online instructions for each purchase. Approximately 30 min should be sufficient. Contact [keesbooij@pasoc.eu](mailto:keesbooij@pasoc.eu) to set a date and time for this.

Contact [keesbooij@pasoc.eu](mailto:keesbooij@pasoc.eu) when the template needs to be tailored to your specific needs, when you need additional  $K_{sw}$  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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