SUPPORTING INFORMATION

Temperature dependence of the organic carbon/water partition ratios (K_{OC}) of volatile methylsiloxanes

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Text S1: Materials

The chemical substances in this study were purchased from the companies presented below: D_4, D_5, 1,4-DCB, α-HCH and Aldrin standards, methanol, potassium hydroxide (KOH) and sodium chloride (NaCl) from Sigma-Aldrich Sweden AB, Stockholm, Sweden; D_6 from Fluorochem, Derbyshire, UK; $^{13}C_4$-D_4, $^{13}C_5$-D_5 and $^{13}C_6$-D_6 from Moravek Biochemicals Inc., Brea, California, USA; polychlorinated biphenyls (PCBs) PCB 28, PCB 52, PCB 53, PCB 101, PCB 118, PCB138, PCB 153, $^{13}C_{12}$-PCB 28, $^{13}C_{12}$-PCB 52, $^{13}C_{12}$-PCB 101, $^{13}C_{12}$-PCB 118, $^{13}C_{12}$-PCB 138 and $^{13}C_{12}$-PCB 153 from Larodan, Solna, Sweden; Isolute ENV+ resin (hydroxylated polystyrene-divinylbenzene copolymer) from Biotage AB (Uppsala, Sweden); dichloromethane (SupraSolv) and *n*-hexane (LiChrosolv) from Merck (Darmstadt, Germany); concentrated sulfuric acid (98 %) from BDH AnalaR (Poole, England). The water was filtered using a Milli-Q system (Merck Millipore, Solna, Sweden). Sediment with an organic carbon content of 6.4 % was collected from Lake Ången, Sweden, and has been used in previous studies in our group[1-2].

Text S2: Modeling

The model we used in this study describes the volatilization of chemicals from the bulk water in the purge-and-trap system using first-order kinetics. The model accounts for degradation and the formation of a pool of chemical that is not available for volatilization from the system.

$$I(t) = (100 - b(t))\mathrm{e}^{-kt} + b(t) \quad \text{(S1)}$$

where I(t) is the percentage of available chemical in bulk water at time (t), k is the volatilization rate constant of the chemical and b(t) is the percentage of the chemical at time t that is not available for volatilization due to formation of a non-available fraction and/or due to degradation. A similar example of this model can be found in the studies of Whelan et al.[3-4]

The formation of the non-available fraction was also described by a first-order kinetic model, which assumed that 100 % of the chemical is available at time 0.

$$b(t) = B(1 - e^{-k_{\mathrm{b}}t}) \quad \text{(S2)}$$

where b(t) is the percentage of the chemical that is not available at time t, B is the maximum percentage of the non-available fraction and k_{b} is the rate constant for formation of the non-available fraction. The model was fit to the observed values for I(t) at various time points using least-squares minimization by optimizing values of k, B and k_{b} in Eq. (S1) and Eq. (S2), with the added constraint that $B \leq 20$ as described by Panagopoulos et al.[1] For the least-squares minimization we used the Solver function in Microsoft Excel. The equations of the model are presented in detail in Panagopoulos et al.[1]

1,4-DCB and α-HCH were used as benchmarking chemicals to calibrate the mass transfer coefficients (*MTC*) of the model at the air-side (*MTC*a) and the water-side (*MTC*w). The K_{AW} and K_{OC} of 1,4-DCB and α-HCH that were used for

88 the calibration of the model are presented in Table S3. The K_{OC} of the
89 benchmark chemicals were calculated using the PP-LFER of Panagopoulos et
90 al.[1] and their K_{AW} were calculated using the PP-LFER of Endo and Goss[5]. K_{OC}
91 measurements can vary by more than an order of magnitude depending on the
92 source and the characteristics of the organic carbon[9-10] and for that reason we
93 chose to work with PP-LFER calculated values than having to choose from a
94 wide range of K_{OC} measurements. The K_{OC} PP-LFER was constructed using a
95 dataset of experimental values for 83 chemicals and it was evaluated for its
96 predictive performance using the cross-validation leave-one-out approach.[1] The
97 K_{AW} of VMS and PCBs used in the modeling calculations are shown in Table S4.
98 The K_{OC} of the benchmarks and the K_{AW} of all chemicals were adjusted for
99 temperature changes using the ΔH_{OW} and ΔH_{AW} calculated by the PP-LFERs of
100 Brown and Wania[6] (Table S5). The K_{AW} values for the VMS compounds are
101 substantially larger than those of the PCBs for all temperatures, suggesting
102 that the characteristic time for transfer from water to air will be dominated by
103 the contribution on the water side of the air-water interface. Therefore, it may
104 not be necessary to know the exact K_{AW} for VMS as long as the K_{AW} is high
105 enough to facilitate immediate transfer of VMS from water to air. Using ΔH_{OW} of
106 Brown and Wania[6] to correct the K_{OC} of the benchmarks from 25 ^{o}C to 5 ^{o}C, the
107 log K_{OC} of 1,4-DCB increased only by 0.18 log units and the log K_{OC} of α-HCH
108 increased by less than 0.01 log units. The calculated ΔH_{OW} of the benchmarks
109 were compared to experimental values found in the literature. The K_{OW} of 1,4-
110 DCB from 25 to 5 ^{o}C increased by 0.19 log units in the study of Bahadur et al.[7]

111 and the K_{OW} of α-HCH from 25 to 5 °C increased by 0.13 log units in the study
112 of Paschke and Schüürmann[8]. We conducted a sensitivity analysis to assess
113 how sensitive our calculations of K_{OC} are to variation in the K_{OC} of the
114 benchmarks. Our sensitivity analysis showed that ± 1 log unit deviation in the
115 K_{OC} of 1,4-DCB resulted in a difference smaller than 0.01 in the calculated K_{OC},
116 and ± 1 log unit deviation in the K_{OC} of α-HCH resulted in a difference smaller
117 than 0.001 in the calculated K_{OC} (Figure S1). The necessary temperature
118 correction of the K_{OC} of the benchmarks is not expected to be larger than 1 log
119 unit and therefore we can safely assume that it will not have a substantial
120 effect on the calculations of K_{OC}.

121

122 Text S3: Volatilization curves and calculations of K_{OC}

123 The volatilization rates for all chemicals from the purge-and-trap system,
124 along with the correlation coefficients (R^2) and the adjusted model parameters
125 k, B, k_b and I_o, are presented in Tables S6, S7, S8 and S9, for 25, 15, 10 and 5
126 °C, respectively. Examples of the volatilization curves of cVMS and lVMS at 5 °C
127 are shown in Figure S2. In the example for D_6 (Figure S2) there is no apparent
128 volatilization after 20 hours because the amount of D_6 in these samples was low
129 compared to the spiked amount of D_6. However, D_6 was quantifiable in all
130 samples and in all cases higher than the blanks. Out of 156 volatilization
131 curves, R^2 was greater than 0.9 in 151 cases, greater than 0.8 in 155 cases and
132 only in one case it was lower than 0.8 (one of the 3 replicates for D_4 at 5 °C,

133 Table S9). The non-available fraction was found to be between 0 and 10 for 137
134 cases and between 10 and 20 for 19 cases. The *MTC*a and the *MTC*w of the air-
135 water interface, which were derived from the 1,4-DCB and α-HCH data are
136 presented in Table S10. There is some variability between the experiments at
137 different temperatures but the replicate measurements of the two mass transfer
138 coefficients at each temperature show only small differences as indicated by the
139 small standard deviations. Variability in the *MTC*a values between experiments
140 at various temperatures can be explained by a difference in the air flow and
141 variability in the *MTC*w values can be explained by a difference in the stirring
142 speed of the water. This variation does not occur in between replicates of the
143 same temperature because all the purge-and-trap systems are connected to the
144 same nitrogen outlet with the same air-flow and all the flasks are placed on the
145 same stirring plate where the stirring speed the same for all. In any case, this
146 variation is controlled by the two benchmark chemicals and therefore it does
147 not affect the calculations of K_{OC}.

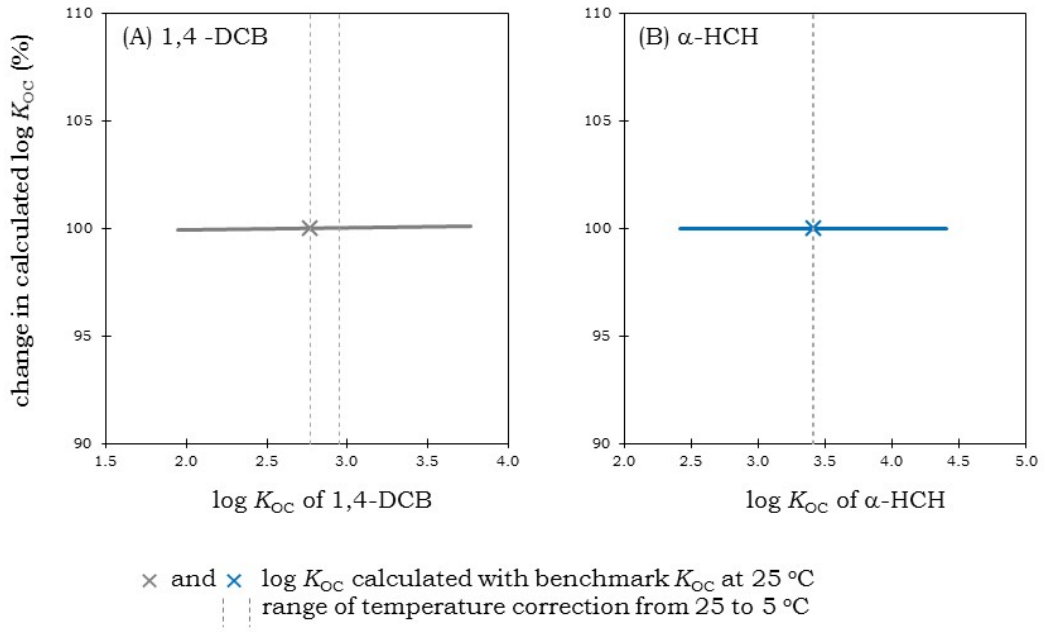
148

149 Text S4: Hydrolysis

150 As VMS are subject to hydrolysis, the rate of hydrolysis of VMS is a matter of
151 concern when one is measuring their K_{OC}. In our modeling calculations we used
152 the half-lives for hydrolysis of D_4, D_5 and D_6 in water at 25 ^{o}C and pH 7, which
153 were calculated by Environment Canada in their assessment reports for D_4, D_5
154 and D_6.[11-13] No published studies were found on the hydrolysis of D_4, D_5, D_6, L_4

155 and L_5 in water and sediment. Environment Canada calculated the half-lives for
156 D_4 and D_5 in water at various temperatures and pH values based on an
157 unpublished report by Kozerski.[11-13] The half-life of D_6 is a read-across value
158 from D_4 and D_5. At pH 7 and 25 °C the values of D_4, D_5 and D_6 were 3.7, 74
159 and 401 days. All values that we used for all temperatures are presented in
160 Table S12.

161



162

163 Figure S1: Sensitivity analysis for the influence of the temperature correction of
164 the benchmarking chemicals on the calculated K_{OC} of the other chemicals.

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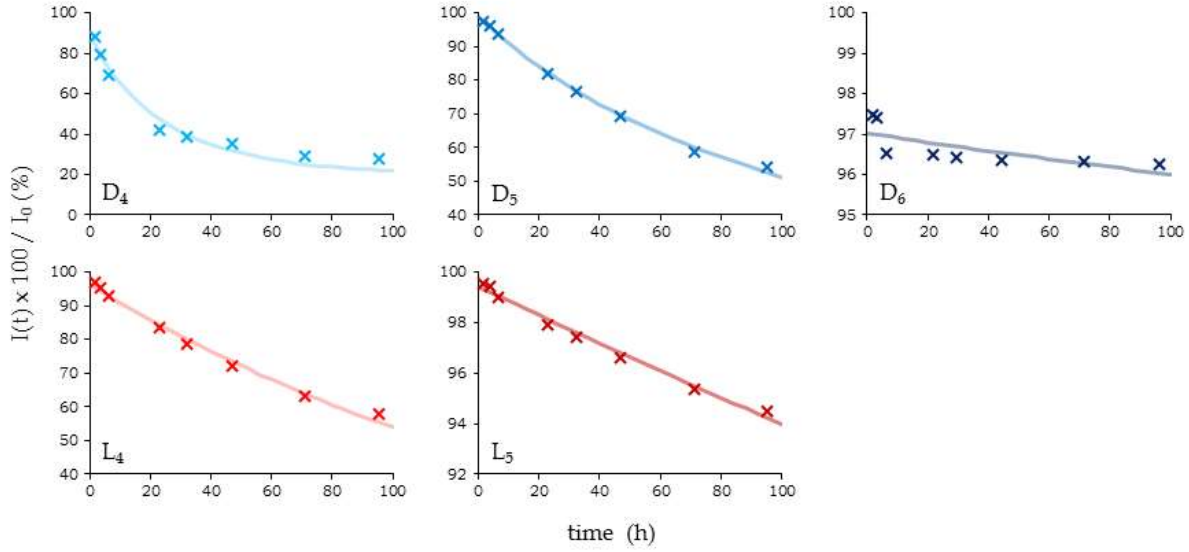

Figure S2: Examples of volatilization curves (observed data and model fits). The figures show the percentage of spiked cyclic and linear volatile methylsiloxanes remaining in the purge-and-trap system as a function of time at 5 °C. The lines are the model fits using Eq. (S2) and Eq. (S3). I(t) is the amount of the chemical that has not volatilized and been trapped by the ENV+ sorbent at time t and I_0 is the amount spiked into the system. The model fitting parameters for Eq. (S2) and Eq. (S3) can be found in Tables S6-S9. Note the different scales of the y axes in the figures. The scales were adjusted so that the fits of the model to the experimental data become clearly visible.

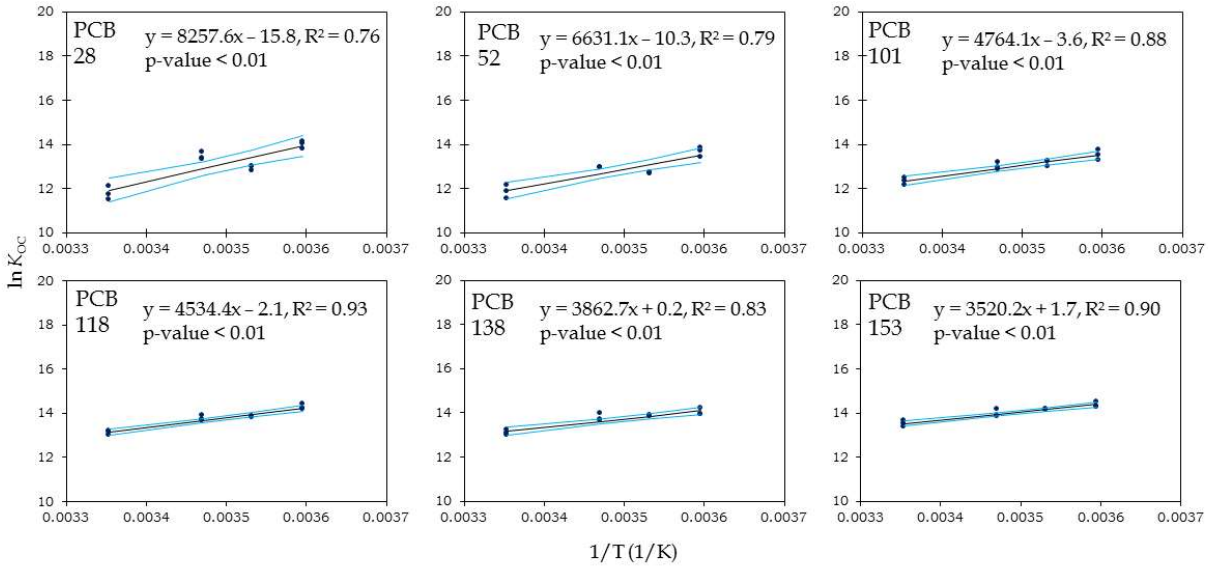

Figure S3: ln K_{OC} as a function of temperature (1/T) for 6 PCBs. The values are presented in ln instead of log so that the figures are in agreement with the the Van't Hoff theory. The dark blue dots represent the ln K_{OC} measurements (n=3) at the different temperatures (total n = 12 per chemical). The black lines are the regression lines and the blue lines are the 95% confidence intervals of the regression lines. From the slopes we calculated the ΔH_{OC} using Eq. (2) and from the intercepts we calculated ΔS_{OC} using Eq. (3).

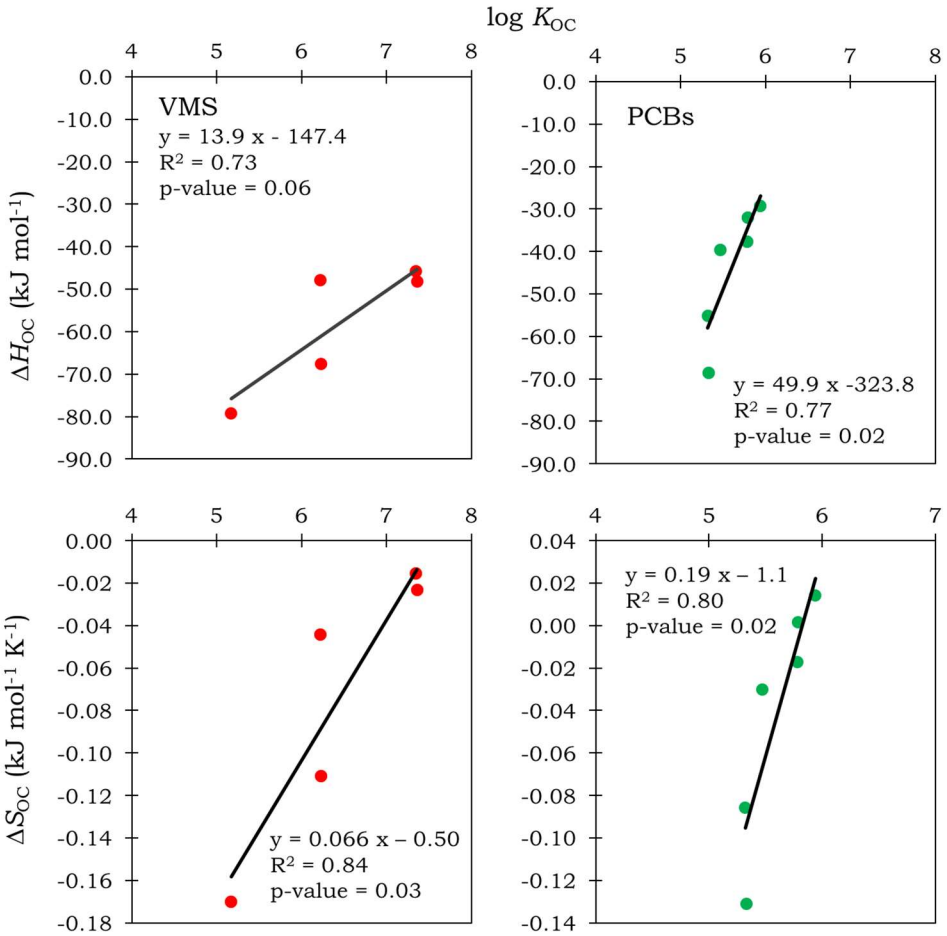

Figure S4: Linear regressions between ΔH_{OC}, ΔS_{OC} and log K_{OC} for VMS and PCBs. VMS are shown in red, PCBs in green and the black lines are the regression lines.

205

206 Table S1: Approximate concentrations in the spiking solution used for spiking
207 the sediment, concentrations of chemicals in the sediment after equilibration
208 and spiking efficiencies.

Chemical	Concentration in spiking solution (ng/μL)	Concentration in sediment (ng/mg)	Spiking efficiency (%)
D4	15000	60	40
D5	10000	60	60
D6	7500	60	80
L4	10000	60	60
L5	7500	60	80
1,4-DCB	2000	5	30
a-HCH	600	5	90
PCBs	600	5	90

209

210

211 Table S2. Average total recoveries of chemicals in the K_{OC} experiments (n = 12
212 for each entry in the table). Recoveries were calculated by adding the amounts
213 of chemical collected from ENV+ and bulk water including sediment, and
214 dividing by the amount of a chemical initially added to the system. The
215 standard deviations are shown in parentheses.

216

	1,4-DCB	D_4	D_5	D_6	L_4	L_5
total recovery (%)	70.1	109.9	112.5	76.2	121.7	82.5
SD (%)	(13.6)	(10.8)	(6.6)	(14.6)	(30.1)	(18.1)

217

	α-HCH	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153
total recovery (%)	73.0	102.9	101.6	83.2	65.9	70.6	77.6
SD (%)	(10.2)	(4.2)	(5.4)	(1.7)	(3.5)	(7.2)	(6.4)

Table S3: log K_{OC} and log K_{AW} of the benchmark chemicals used in the calibration of the *MTC*a and *MTC*w of the model.

	T (°C)	25	21	15	10	5
log K_{OC}	1,4-DCB	2.80	2.77	2.87	2.91	2.95
	α-HCH	3.41	3.41	3.41	3.41	3.41
log K_{AW}	1,4-DCB	-0.76	-0.69	-0.95	-1.06	-1.16
	α-HCH	-3.90	-3.72	-4.36	-4.61	-4.86

Table S4: log K_{AW} of VMS and PCBs used in the modeling calculations.

	log K_{AW}				
T (°C)	25	21	15	10	5
D_4	3.09	2.92	2.51	2.29	2.06
D_5	3.38	3.18	2.65	2.37	2.08
D_6	3.36	3.10	2.44	2.09	1.73
L_4	2.78	2.58	2.06	1.79	1.50
L_5	3.11	2.87	2.24	1.91	1.57
PCB 28	-2.15	-2.28	-2.61	-2.79	-2.97
PCB 52	-2.22	-2.36	-2.71	-2.90	-3.09
PCB 101	-2.64	-2.78	-3.13	-3.32	-3.52
PCB 118	-2.75	-2.89	-3.24	-3.43	-3.62
PCB 153	-2.68	-2.83	-3.20	-3.40	-3.61
PCB 138	-2.93	-3.08	-3.45	-3.64	-3.84

Table S5: ΔH_{AW} and ΔH_{OW} used to correct the chemicals' K_{AW} and K_{OC}. The ΔH values were calculated using the PP-LFER of Brown and Wania[6].

	ΔHaw	ΔHow
1,4-DCB	31.54	-12.12
α-HCH	76.45	-0.55
D_4	68.47	
D_5	87.28	
D_6	108.83	
L_4	85.18	
L_5	103.25	
PCB 28	55.25	
PCB 52	57.81	
PCB 101	58.57	
PCB 118	58.52	
PCB 153	61.80	
PCB 138	61.01	

Table S6: Values for k *(% h^{-1})*, B *(%)*, k_b *(% h^{-1})*, I_o (%) and R^2 for all chemicals involved in the K_{OC} experiments at 25 °C.

25 °C	D_4			D_5			D_6		
replicate	1	2	3	1	2	3	1	2	3
k	-1.10E-01	-1.11E-01	-7.38E-02	-1.52E-02	-1.60E-02	-1.00E-02	-1.85E-03	-6.44E-04	-1.04E-03
B	0.00E+00	1.70E+00	0.00E+00	2.00E+01	2.00E+01	1.10E-01	0.00E+00	0.00E+00	1.05E-01
k_b	-1.25E-01	-1.65E-01	-4.46E-04	-5.89E-02	-3.66E-02	-3.46E-03	0.00E+00	0.00E+00	-3.32E-03
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	7.27E+01	8.87E+01	9.51E+01	8.92E+01	8.98E+01	9.47E+01	9.12E+01	9.81E+01	9.89E+01
R^2	9.84E-01	9.30E-01	9.54E-01	9.65E-01	9.11E-01	9.80E-01	9.87E-01	9.60E-01	9.71E-01

	L_4			L_5			1,4-DCB			a-HCH		
replicate	1	2	3	1	2	3	1	2	3	1	2	3
k	-9.96E-03	-3.89E-02	-2.08E-02	-1.95E-03	-1.34E-03	-1.79E-03	-2.08E-01	-2.90E-01	-3.77E-01	-1.88E-03	-4.12E-03	-3.00E-03
B	0.00E+00	0.00E+00	2.00E+01	0.00E+00	0.00E+00	1.05E-01	0.00E+00	0.00E+00	1.04E-01	0.00E+00	0.00E+00	2.00E+01
k_b	0.00E+00	0.00E+00	-2.28E-01	0.00E+00	0.00E+00	-3.32E-03	0.00E+00	0.00E+00	-3.30E-03	0.00E+00	0.00E+00	-2.00E-02
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.50E+01	7.61E+01	9.86E+01	9.11E+01	9.66E+01	9.84E+01	8.05E+01	8.45E+01	9.53E+01	9.64E+01	9.56E+01	9.57E+01
R^2	9.70E-01	9.03E-01	9.54E-01	9.77E-01	9.80E-01	9.84E-01	9.93E-01	9.94E-01	9.90E-01	8.46E-01	9.39E-01	8.93E-01

	PCB 28			PCB 52			PCB 101		
replicate	1	2	3	1	2	3	1	2	3
k	-2.39E-02	-3.05E-02	-3.58E-02	-2.00E-02	-2.44E-02	-3.03E-02	-7.71E-03	-6.96E-03	-8.93E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.49E+01	9.75E+01	9.73E+01	9.63E+01	9.83E+01	9.89E+01	9.85E+01	9.79E+01	9.83E+01
R^2	9.96E-01	9.97E-01	9.98E-01	9.97E-01	9.97E-01	9.99E-01	9.95E-01	9.96E-01	9.98E-01

	PCB 118			PCB 138			PCB 153		
replicate	1	2	3	1	2	3	1	2	3
k	-3.16E-03	-3.05E-03	-3.65E-03	-2.32E-03	-2.03E-03	-2.54E-03	-2.68E-03	-2.31E-03	-2.94E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.70E+01	9.71E+01	9.71E+01	9.82E+01	9.83E+01	9.87E+01	9.81E+01	9.81E+01	9.84E+01
R^2	9.86E-01	9.87E-01	9.87E-01	9.92E-01	9.91E-01	9.95E-01	9.91E-01	9.89E-01	9.94E-01

Table S7: Values for k *(% h^{-1})*, B *(%)*, k_b *(% h^{-1})*, I_o (%) and R^2 for all chemicals involved in the K_{OC} experiments at 15 °C.

15 °C	D_4			D_5			D_6		
replicate	1	2	3	1	2	3	1	2	3
k	-5.59E-02	-7.49E-02	-6.34E-02	-4.53E-03	-9.07E-03	-6.19E-03	-3.08E-04	-5.55E-04	-4.83E-04
B	1.06E+01	0.00E+00	8.90E+00	2.00E+01	2.00E+01	2.00E+01	0.00E+00	0.00E+00	1.05E-01
k_b	-6.26E-01	-1.70E-01	-6.34E-01	-2.00E-02	-2.17E-01	-1.91E-02	0.00E+00	0.00E+00	-3.32E-03
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.41E+01	8.46E+01	8.67E+01	1.00E+02	9.71E+01	9.74E+01	1.00E+02	1.00E+02	9.97E+01
R^2	9.74E-01	9.81E-01	9.74E-01	9.75E-01	9.68E-01	9.67E-01	9.61E-01	9.58E-01	9.71E-01

	L_4			L_5			1,4-DCB			a-HCH		
replicate	1	2	3	1	2	3	1	2	3	1	2	3
k	-3.44E-03	-6.91E-03	-5.92E-03	-2.93E-04	-5.27E-04	-4.49E-04	-9.29E-02	-1.23E-01	-1.88E-01	-1.62E-03	-1.56E-03	-1.69E-03
B	0.00E+00	0.00E+00	2.00E+01	0.00E+00	0.00E+00	1.05E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.00E+01
k_b	0.00E+00	0.00E+00	-1.93E-02	0.00E+00	0.00E+00	-3.32E-03	0.00E+00	0.00E+00	-2.24E-01	0.00E+00	0.00E+00	-2.41E-02
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.89E+01	9.65E+01	9.78E+01	9.99E+01	9.98E+01	9.95E+01	7.52E+01	7.10E+01	6.09E+01	9.85E+01	9.84E+01	9.81E+01
R^2	9.79E-01	9.67E-01	9.70E-01	9.71E-01	9.67E-01	9.75E-01	9.91E-01	9.93E-01	9.99E-01	9.73E-01	9.75E-01	9.74E-01

	PCB 28			PCB 52			PCB 101		
replicate	1	2	3	1	2	3	1	2	3
k	-8.96E-03	-1.13E-02	-1.16E-02	-1.34E-02	-1.34E-02	-1.33E-02	-5.46E-03	-6.85E-03	-6.61E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.08E+01	8.76E+01	8.81E+01	9.13E+01	9.13E+01	9.15E+01	9.86E+01	9.63E+01	9.62E+01
R^2	9.40E-01	9.18E-01	9.36E-01	9.53E-01	9.53E-01	9.63E-01	9.84E-01	9.81E-01	9.85E-01

	PCB 118			PCB 138			PCB 153		
replicate	1	2	3	1	2	3	1	2	3
k	-2.51E-03	-2.97E-03	-2.85E-03	-1.51E-03	-2.02E-03	-1.93E-03	-2.11E-03	-2.75E-03	-2.62E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.81E+01	9.71E+01	9.68E+01	9.93E+01	9.87E+01	9.84E+01	9.93E+01	9.84E+01	9.80E+01
R^2	9.87E-01	9.85E-01	9.86E-01	9.78E-01	9.85E-01	9.88E-01	9.80E-01	9.84E-01	9.88E-01

Table S8: Values for k *(% h^{-1})*, B *(%)*, k_b *(% h^{-1})*, I_o (%) and R^2 for all chemicals involved in the K_{OC} experiments at 10 °C.

10 oC	D_4			D_5			D_6		
replicate	1	2	3	1	2	3	1	2	3
k	-5.58E-02	-3.41E-02	-1.07E-01	-1.29E-02	-1.40E-02	-1.17E-02	-9.80E-04	-7.87E-04	-7.36E-04
B	2.86E-01	0.00E+00	5.44E-03	7.70E+00	3.31E+00	5.92E+00	0.00E+00	0.00E+00	1.05E-01
k_b	-1.26E-01	-1.70E-01	-4.46E-04	-2.73E-02	-1.76E-01	-1.21E-01	0.00E+00	0.00E+00	-3.32E-03
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.95E+01	1.00E+02	1.08E+02	8.41E+01	8.72E+01	8.68E+01	9.17E+01	9.28E+01	9.78E+01
R^2	9.97E-01	9.57E-01	9.98E-01	9.96E-01	9.78E-01	9.83E-01	9.84E-01	9.21E-01	9.87E-01

	L_4			L_5			1,4-DCB			a-HCH		
replicate	1	2	3	1	2	3	1	2	3	1	2	3
k	-4.88E-03	-4.56E-03	-7.72E-03	-8.67E-04	-4.05E-04	-6.28E-04	-1.64E-01	-1.74E-01	-2.07E-01	-7.02E-04	-4.88E-04	-6.95E-04
B	0.00E+00	0.00E+00	2.00E+01	0.00E+00	0.00E+00	1.05E-01	0.00E+00	0.00E+00	2.57E+00	0.00E+00	0.00E+00	2.00E+01
k_b	0.00E+00	0.00E+00	-5.11E-02	0.00E+00	0.00E+00	-3.32E-03	0.00E+00	0.00E+00	-2.16E-01	0.00E+00	0.00E+00	-9.63E-03
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	8.40E+01	7.71E+01	9.18E+01	8.97E+01	9.15E+01	9.70E+01	9.00E+01	9.57E+01	1.05E+02	9.92E+01	9.94E+01	9.98E+01
R^2	9.49E-01	9.95E-01	9.59E-01	9.85E-01	9.87E-01	9.85E-01	9.87E-01	9.93E-01	1.00E+00	9.79E-01	9.67E-01	9.93E-01

	PCB 28			PCB 52			PCB 101		
replicate	1	2	3	1	2	3	1	2	3
k	-7.53E-03	-6.54E-03	-6.51E-03	-6.98E-03	-6.51E-03	-6.62E-03	-2.19E-03	-1.80E-03	-1.81E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.70E+01	9.74E+01	9.61E+01	9.82E+01	9.90E+01	9.77E+01	1.00E+02	9.94E+01	9.91E+01
R^2	9.92E-01	9.86E-01	9.78E-01	9.98E-01	9.96E-01	9.92E-01	9.94E-01	9.99E-01	9.96E-01

	PCB 118			PCB 138			PCB 153		
replicate	1	2	3	1	2	3	1	2	3
k	-8.57E-04	-8.20E-04	-8.25E-04	-5.09E-04	-4.92E-04	-5.13E-04	-6.71E-04	-6.46E-04	-6.45E-04
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.79E+01	9.79E+01	9.78E+01	9.95E+01	9.95E+01	9.97E+01	9.80E+01	9.80E+01	9.75E+01
R^2	9.85E-01	9.90E-01	9.86E-01	9.86E-01	9.93E-01	9.89E-01	9.81E-01	9.86E-01	9.86E-01

Table S9: Values for k *(% h^{-1})*, B *(%)*, k_b *(% h^{-1})*, I_o (%) and R^2 for all chemicals involved in the K_{OC} experiments at 5 °C.

5 °C	D_4			D_5			D_6		
replicate	1	2	3	1	2	3	1	2	3
k	-3.50E-02	-8.43E-03	-1.06E-02	-8.69E-03	-5.23E-03	-6.26E-03	-4.34E-04	-1.04E-03	-3.54E-04
B	2.00E+01	2.00E+01	5.44E-03	2.00E+01	5.00E+00	2.00E+01	0.00E+00	0.00E+00	1.05E-01
k_b	-4.87E-02	-1.00E+00	-4.46E-04	-1.94E-02	-1.00E+00	-1.00E+00	0.00E+00	0.00E+00	-3.32E-03
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	8.94E+01	7.60E+01	8.13E+01	9.88E+01	8.87E+01	9.58E+01	9.99E+01	9.98E+01	9.99E+01
R^2	9.72E-01	7.75E-01	8.19E-01	9.97E-01	8.70E-01	9.42E-01	9.86E-01	9.87E-01	9.91E-01

	L_4			L_5			1,4-DCB			a-HCH		
replicate	1	2	3	1	2	3	1	2	3	1	2	3
k	-5.80E-03	-4.05E-03	-4.96E-03	-5.63E-04	-1.32E-03	-5.76E-04	-8.10E-02	-8.71E-02	-8.90E-02	-3.19E-04	-2.17E-04	-3.66E-04
B	0.00E+00	0.00E+00	2.00E+01	0.00E+00	0.00E+00	2.00E+01	0.00E+00	0.00E+00	1.01E+00	0.00E+00	0.00E+00	2.00E+01
k_b	0.00E+00	0.00E+00	-2.03E-02	0.00E+00	0.00E+00	-1.84E-02	0.00E+00	0.00E+00	-4.91E-01	0.00E+00	0.00E+00	-1.48E-02
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.65E+01	8.94E+01	9.66E+01	9.94E+01	9.81E+01	9.96E+01	9.33E+01	8.93E+01	9.73E+01	1.00E+02	9.99E+01	1.00E+02
R^2	9.91E-01	9.14E-01	9.64E-01	9.86E-01	9.74E-01	9.96E-01	9.99E-01	9.98E-01	9.98E-01	9.81E-01	9.71E-01	9.78E-01

	PCB 28			PCB 52			PCB 101		
replicate	1	2	3	1	2	3	1	2	3
k	-6.17E-03	-4.84E-03	-5.20E-03	-6.19E-03	-4.78E-03	-5.24E-03	-2.78E-03	-2.15E-03	-2.43E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	1.00E+02	9.91E+01	9.85E+01	1.00E+02	9.91E+01	9.85E+01	9.91E+01	9.86E+01	9.81E+01
R^2	9.88E-01	9.85E-01	9.74E-01	9.89E-01	9.86E-01	9.79E-01	9.85E-01	9.81E-01	9.78E-01

	PCB 118			PCB 138			PCB 153		
replicate	1	2	3	1	2	3	1	2	3
k	-1.26E-03	-1.07E-03	-1.21E-03	-9.23E-04	-7.69E-04	-9.38E-04	-1.20E-03	-1.01E-03	-1.17E-03
B	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
k_b	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
b_o	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
I_o	9.80E+01	9.80E+01	9.75E+01	9.82E+01	9.82E+01	9.76E+01	9.82E+01	9.81E+01	9.75E+01
R^2	9.67E-01	9.54E-01	9.49E-01	9.50E-01	9.31E-01	9.39E-01	9.65E-01	9.52E-01	9.47E-01

Table S10: Averages and standard deviations of *MTC*a and *MTC*w values for each experiment.

		*MTC*a	*MTC*w
25 °C	average	1.930E+00	3.626E-02
	SD	4.444E-01	6.695E-03
15 °C	average	4.298E+00	1.330E-02
	SD	2.351E-01	5.800E-03
10 °C	average	2.877E+00	2.079E-02
	SD	5.945E-01	2.861E-03
5 °C	average	2.312E+00	9.439E-03
	SD	6.116E-01	6.652E-04

Table S11: Measured log K_{OC} (n = 3) for all chemicals at four different temperatures (25, 15, 10 and 5 °C). The standard errors of the measurements are shown in parentheses.

	log K_{OC}							
	25 °C	SE	15 °C	SE	10 °C	SE	5 °C	SE
D4	5.20	(0.08)	5.28	(0.07)	5.34	(0.22)	6.38	(0.25)
D5	6.20	(0.07)	6.16	(0.02)	6.53	(0.09)	6.79	(0.07)
D6	7.32	(0.13)	7.38	(0.04)	7.72	(0.08)	7.91	(0.15)
L4	6.01	(0.18)	6.62	(0.10)	6.54	(0.08)	6.93	(0.05)
L5	7.12	(0.05)	7.74	(0.08)	7.52	(0.10)	7.76	(0.12)
PCB28	5.11	(0.08)	5.84	(0.04)	5.61	(0.03)	6.08	(0.04)
PCB52	5.15	(0.08)	5.63	(0.00)	5.51	(0.01)	5.93	(0.05)
PCB101	5.35	(0.04)	5.65	(0.04)	5.71	(0.03)	5.87	(0.05)
PCB118	5.69	(0.03)	5.98	(0.03)	6.00	(0.01)	6.19	(0.03)
PCB138	5.68	(0.03)	5.97	(0.04)	6.02	(0.01)	6.08	(0.04)
PCB153	5.87	(0.03)	6.07	(0.04)	6.15	(0.01)	6.23	(0.03)

265 Table S12: Half-lives for VMS used in the calculations of K_{OC}.

T (oC)	D_4 half-life (d)	D_5 half-life (d)	D_6 half-life (d)	L_4 half-life (d)[d]	L_5 half-life (d)[d]
25	4[a]	74[a]	401[c]	74	401
15	12[b]	311[b]	685[b]	311	685
10	21[a]	395[a]	769[b]	395	769
5	45[a]	733[a]	1421[b]	733	1421

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267 [a] Data calculated by Environment Canada[11-13] based on measurements in an
268 unpublished report by Kozerski. [b] Read-across calculations in this study. [c]Read-
269 across calculations by Environment Canada. [d]Due to the lack of data for L_4 and
270 L_5, we used the corresponding half-lives for D_5 and D_6.

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