Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

Electronic Supplementary Information

Silicone passive equilibrium samplers as 'chemometers' in eel and sediment of a Swedish lake

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Text S1.

The chemical activity concept. A definition of the chemical activity concept, how chemical activity can be measured and used is described in detail in *Reichenberg & Mayer 2006*[1]; therefore we focus on some basic information. Chemical activity is directly related to the chemical potential of a compound, and it is particularly useful for studying and predicting spontaneous processes that the compound may be subject to. General rules are i) that spontaneous physicochemical processes such as diffusion proceed from high to low chemical activity, and ii) that a thermodynamic equilibrium is established at equal chemical activity, which is the basis of the equilibrium partitioning theory[2].

Chemical activity is a unitless measure with values ranging from zero (i.e., no chemical activity) to one (i.e., saturated with pure compound in liquid state). In contrast to the related concept of the freely dissolved concentration in water, chemical activity is not limited to a specific medium. Equilibrium sampling devices[3] such as solid-phase microextraction fibers or micrometer-thin coatings of various polymers can be used to measure chemical activity. In our work, thin silicone films are brought into contact with an environmental medium to transfer its chemical activity into the silicone. The concentration of the compound in the silicone (C_{Silicone}) can then be measured, and the chemical activity (a) can be calculated using activity coefficients (γ) according to:

$$a = \gamma_{\text{Silicone}} * C_{\text{Silicone}}.$$

One of the applications of chemical activity described by *Reichenberg & Mayer*[1] are measurements of chemical activity to study and predict bioconcentration in sediment organisms. For relatively small organisms living in close proximity to the sediment, the chemical activity in the organism will be controlled by (equilibrium) partitioning from the sediment. Furthermore, the authors propose to measure and compare chemical activities in an organism and its surrounding medium[1] in order to distinguish between equilibrium partitioning (similar a in both media), metabolism or kinetic uptake (lower a in the organism than in the medium) and biomagnification via the feed (higher a in the organism). To the best of our knowledge, the parallel measurement of chemical activities in biota and sediment from one ecosystem is described for the first time in this manuscript. For additional information on the chemical activity concept, see *refs.* [1] and [4].

References

(1) Reichenberg, F.; Mayer, P. *Environ. Toxicol. Chem.* **2006**, 25, 1239-1245.

(2) Di Toro, D.M.; Zarba, C.S.; Hansen, D.J.; Berry, W.J.; Swartz, R.C.; Cowan, C.E.; Pavlou, S.P.; Allen, H.E.; Thomas, N.A.; Paquin, P.R. *Environ. Toxicol. Chem*. **1991**, 10, 1541-1583.

(3) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. *Environ. Sci. Technol.* **2003**, 37, 184A-191A.

(4) Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. Environmental Organic Chemistry. John Wiley, New York, NY, USA, **1993**.

Text S2.

Calculation of the lipid/OC partition ratios ($K_{\mathrm{Lip/OC}}$). We assessed the differences in the sorptive capacities of biota lipids and sediment organic carbon by comparing literature-based lipid/water partition ratios ($K_{\mathrm{Lip/W}}$, derived from equation 1):

$$K_{\mathrm{Lip/W}} = K_{\mathrm{Sil/W}}{}^{1} * K_{\mathrm{Lip/Sil}}{}^{2} \qquad (1)$$

and OC/water partition ratios (K_{OC}, derived from equation 2) from the Lake Ången data:

$$K_{\mathrm{OC}} = C_{\mathrm{Sed,OC}} \,/\, C_{\mathrm{Sed,free}}$$

$$K_{\mathrm{OC}} = C_{\mathrm{Sed,OC}} \,/\, (C_{\mathrm{Sil,sed}} \,/\, K_{\mathrm{Sil/W}}{}^{1}) \qquad (2)$$

Differences in the silicone materials were taken into account by transforming all data to an SSP-M823 basis, the same polymer as used for the $K_{\mathrm{Lip/Sil}}$ data set[2] and the eel sampling. Firstly, the average literature $K_{\mathrm{Sil/W}}$ data for the silicone Altesil[1] were translated to SSP-M823 by division by $K_{\mathrm{Altesil/SSP}}$[3]. The $K_{\mathrm{Altesil/SSP}}$ data were 1.07 (HCB), 1.13 (PCB 180), 1.16 (PCB 153), 1.17 (PCBs 52 and 101), 1.18 (PCB 28), 1.19 (PCB 118) and 1.20 (PCB 138).[3] Secondly, $C_{\mathrm{Sil,sed}}$ obtained with the silicone DC1-2577 were translated to SSP-M823 by division by $K_{\mathrm{DC/SSP}}$[3].

The ratios of $K_{\mathrm{Lip/W}}$ and K_{OC} (i.e. the lipid/OC partition ratios, $K_{\mathrm{Lip/OC}}$) were between 29.3 (PCB 118) and 49.7 (PCB 180) (on average 38.9) for the PCBs with 5 to 7 chlorines.

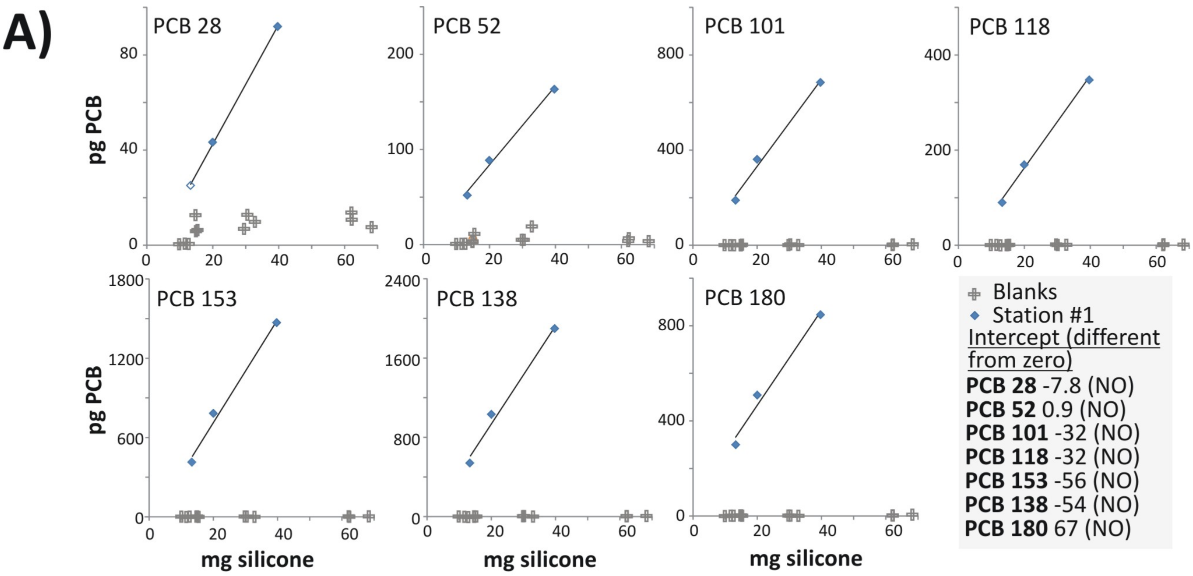
References

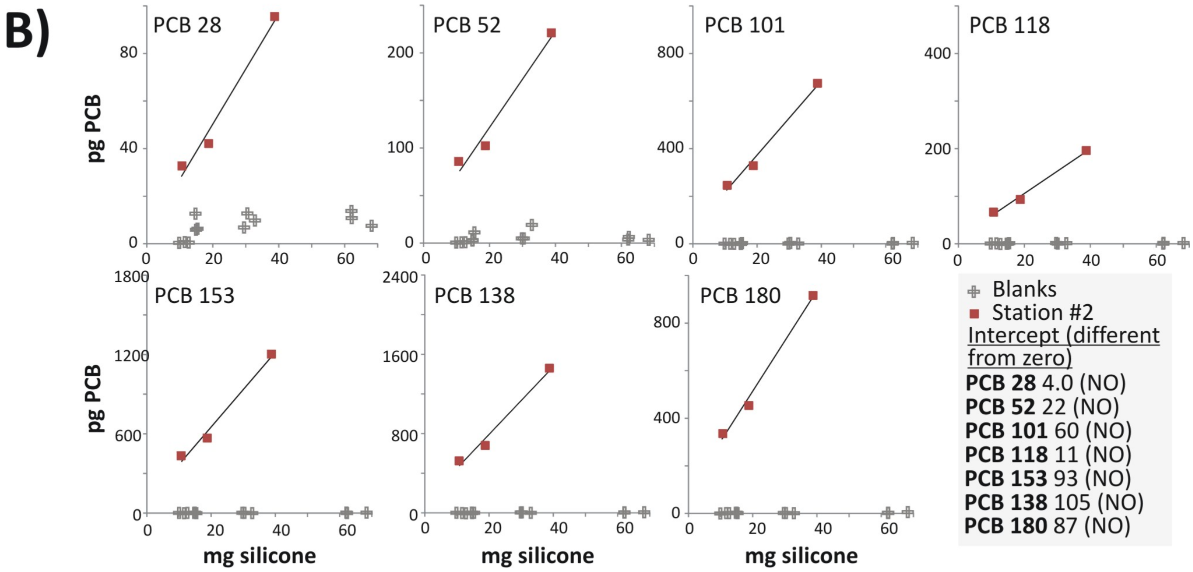
(1) Smedes, F.; Geertsma, R.W.; van der Zande, T.; Booij, K. *Environ. Sci. Technol*. **2009**, 43, 7047-7054.

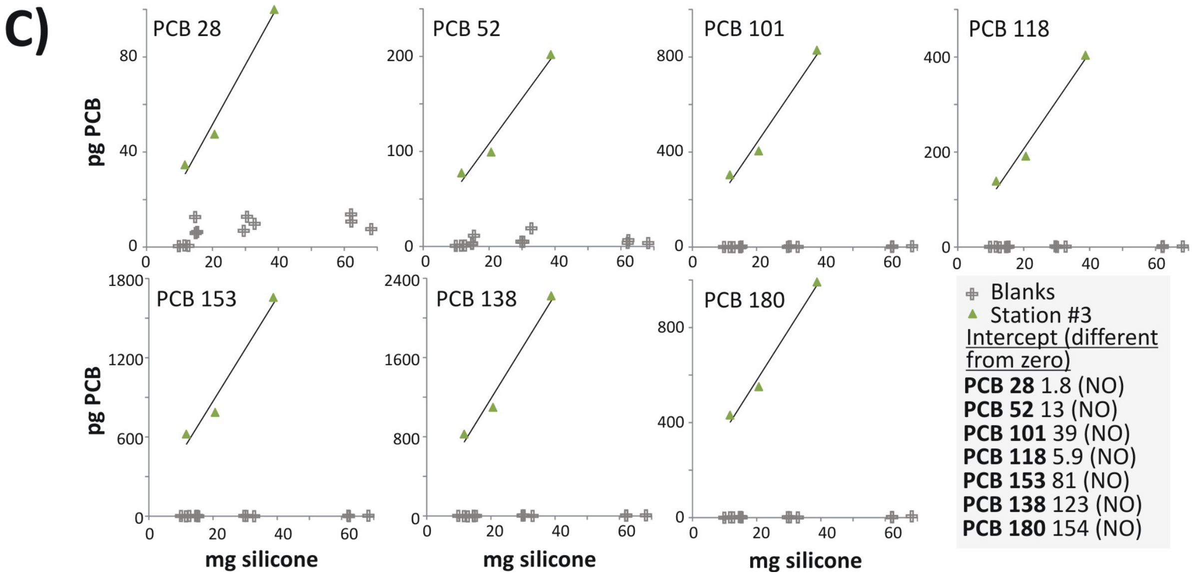
(2) Jahnke, A.; McLachlan, M.S.; Mayer, P. *Chemosphere* **2008**, 73, 1575-1581.

(3) Gilbert, D.; Witt, G.; Smedes, F.; Mayer, P. *Manuscript in preparation*.

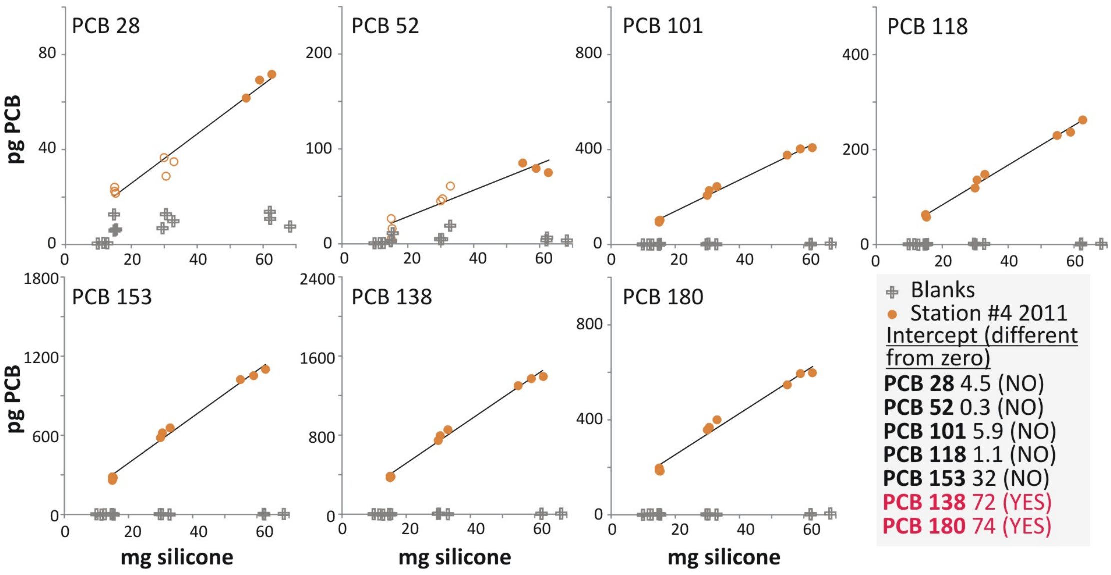
Figure S1. Mass [pg] of the individual 'indicator' PCBs vs. silicone mass [mg] of the glass jar coatings equilibrated with Lake Ången sediment from the different stations and sampling events: A) Station #1, B) Station #2, C) Station #3, D) Station #4 sampled in 2011, E) Station #4 sampled in 2012, F) Station #5. Blanks are also shown. Open symbols represent data below the method quantification limits (<MQL, Table S3). Linear regressions are shown, and the intercepts are listed. In cases where the intercept is statistically different from zero (ANOVA), the data is highlighted in red (see PCBs 138 and 180 in panel D), and PCB 180 in panel F).


A)
PCB 28
PCB 52
PCB 101
PCB 118
PCB 153
PCB 138
PCB 180
pg PCB
mg silicone
0
20
40
60
80
100
200
400
600
800
1200
1600
1800
2400
Blanks
Station #1
Intercept (different from zero)
PCB 28 -7.8 (NO)
PCB 52 0.9 (NO)
PCB 101 -32 (NO)
PCB 118 -32 (NO)
PCB 153 -56 (NO)
PCB 138 -54 (NO)
PCB 180 67 (NO)


B)
PCB 28
PCB 52
PCB 101
PCB 118
PCB 153
PCB 138
PCB 180
pg PCB
mg silicone
0
20
40
60
80
100
200
400
600
800
1200
1600
1800
2400
Blanks
Station #2
Intercept (different from zero)
PCB 28 4.0 (NO)
PCB 52 22 (NO)
PCB 101 60 (NO)
PCB 118 11 (NO)
PCB 153 93 (NO)
PCB 138 105 (NO)
PCB 180 87 (NO)


C)
PCB 28
PCB 52
PCB 101
PCB 118
PCB 153
PCB 138
PCB 180
pg PCB
mg silicone
0
20
40
60
80
100
200
400
600
800
1200
1600
1800
2400
Blanks
Station #3
Intercept (different from zero)
PCB 28 1.8 (NO)
PCB 52 13 (NO)
PCB 101 39 (NO)
PCB 118 5.9 (NO)
PCB 153 81 (NO)
PCB 138 123 (NO)
PCB 180 154 (NO)

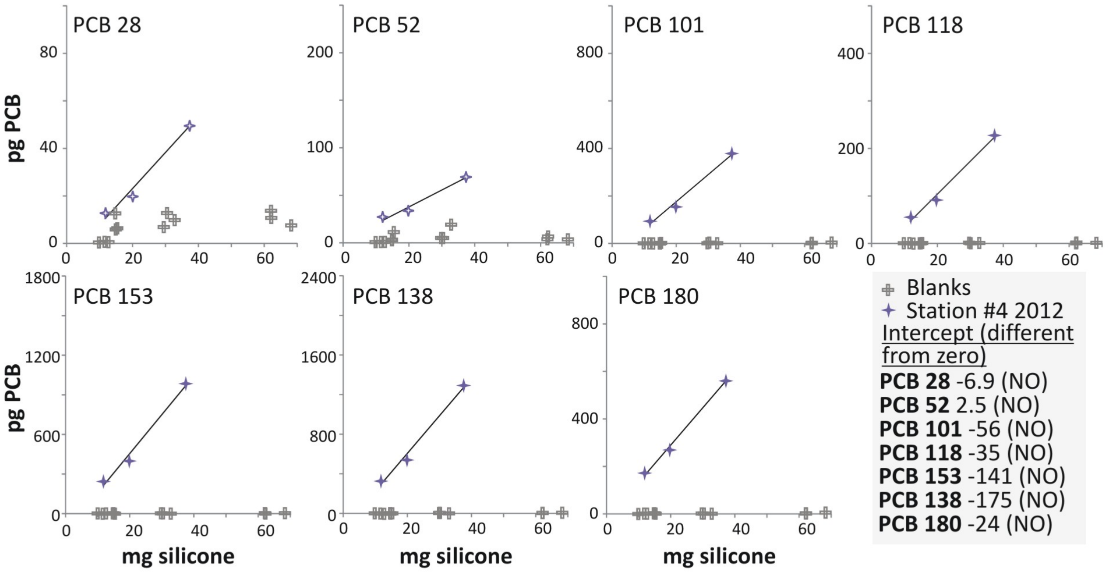
D)



Blanks
● Station #4 2011
Intercept (different from zero)

PCB 28 4.5 (NO)
PCB 52 0.3 (NO)
PCB 101 5.9 (NO)
PCB 118 1.1 (NO)
PCB 153 32 (NO)
PCB 138 72 (YES)
PCB 180 74 (YES)

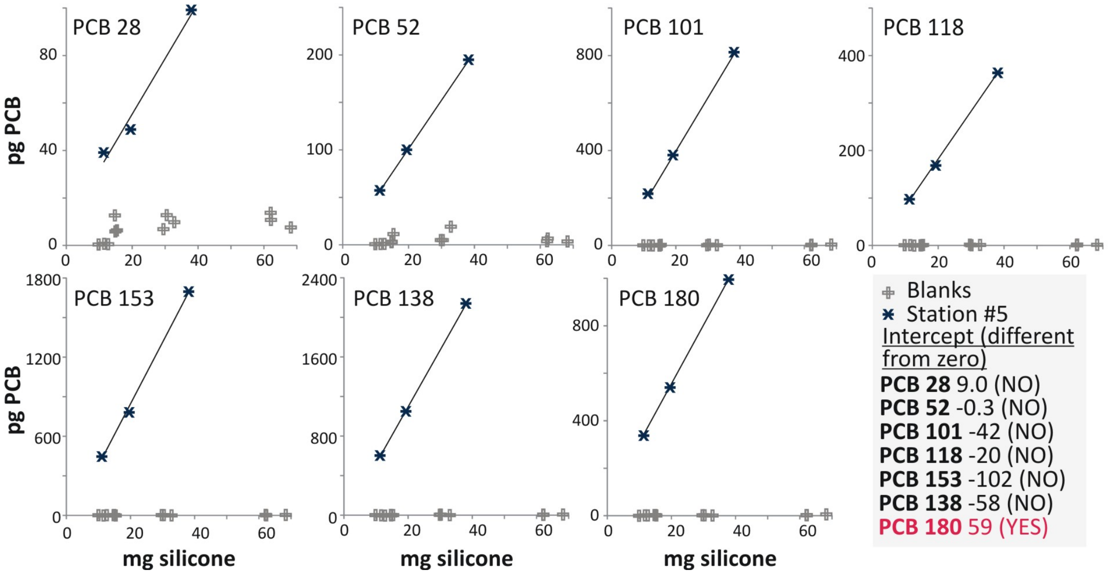
E)



Blanks
Station #4 2012
Intercept (different from zero)

PCB 28 -6.9 (NO)
PCB 52 2.5 (NO)
PCB 101 -56 (NO)
PCB 118 -35 (NO)
PCB 153 -141 (NO)
PCB 138 -175 (NO)
PCB 180 -24 (NO)

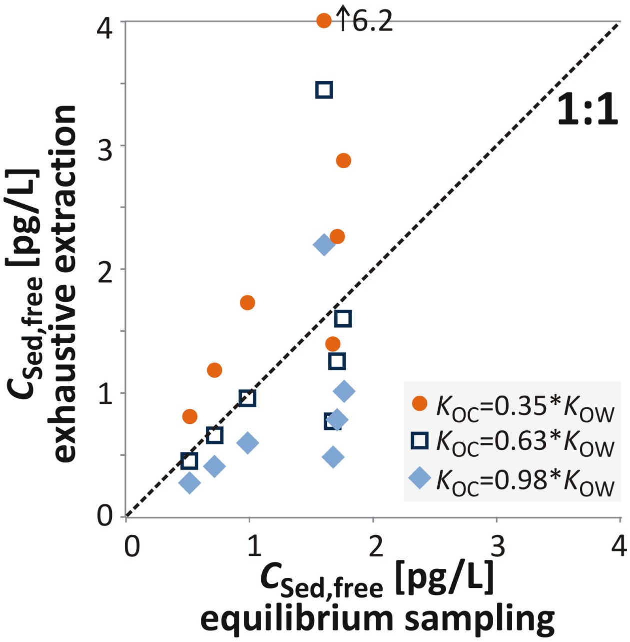
F)



Blanks
Station #5
Intercept (different from zero)

PCB 28 9.0 (NO)
PCB 52 -0.3 (NO)
PCB 101 -42 (NO)
PCB 118 -20 (NO)
PCB 153 -102 (NO)
PCB 138 -58 (NO)
PCB 180 59 (YES)

Figure S2. Freely dissolved concentrations of the model chemicals in interstitial pore water [$C_{\mathrm{Sed,free}}$, pg/L] of the sediment from station #4 at 20 °C estimated from the total extraction sediment data [$C_{\mathrm{Sed,OC}}$ / K_{OC}] vs. the coated glass jar approach [$C_{\mathrm{Sil,sed}}$ / $K_{\mathrm{Sil/W}}$[1]].[2] The K_{OC} data were derived from K_{OW}[3] using three different generic relationships[4-6]. See Table S6 for the $C_{\mathrm{Sed,free}}$ data.



References

(1) Smedes, F.; Geertsma, R.W.; van der Zande, T.; Booij, K. *Environ. Sci. Technol*. **2009**, 43, 7047-7054.

(2) Jahnke, A.; Mayer, P.; McLachlan, M.S. *Environ. Sci. Technol.* **2012***,* 46, 10114-10122.

(3) Schenker, U.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. *Environ. Sci. Technol*. **2005**, 39, 8434-8441.

(4) Seth, R.; Mackay, D.; Muncke, J. *Environ. Sci. Technol*. **1999**, 33, 2390-2394.

(5) Karickhoff, S.W.; Brown, D.S.; Scott, T.A. *Water Res.* **1979**, 13, 241-248.

(6) Di Toro, D.M.; Zarba, C.S.; Hansen, D.J.; Berry, W.J.; Swartz, R.C.; Cowan, C.E.; Pavlou, S.P.; Allen, H.E.; Thomas N.A.; Paquin, P.R. *Environ. Toxicol. Chem*. **1991**, 10, 1541-1583.

Table S1. List of the most important abbreviations used throughout the manuscript, together with several key formulas.

Abbreviation	**Relevant information**
$C_{\mathrm{Sil,sed}}$	Chemical concentration in the silicone equilibrated with sediment
$C_{\mathrm{Sed,lip}}$	Concentrations in lipids at equilibrium with the sediment: $C_{\mathrm{Sed,lip}} = C_{\mathrm{Sil,sed}} * K_{\mathrm{Lip/Sil}}$
$K_{\mathrm{Lip/Sil}}$	Lipid/silicone partition ratio
$K_{\mathrm{Sil/W}}$	Silicone/water partition ratio
$K_{\mathrm{DC/SSP}}$	DC1-2577/SSP-M 823 partition ratio
$C_{\mathrm{Sil,eel}}$	Chemical concentration in the silicone equilibrated with eel
$C_{\mathrm{Lip,eq}}$	Equilibrium partitioning concentrations in lipids: $C_{\mathrm{Lip,eq}} = C_{\mathrm{Sil,eel}} * D_{\mathrm{Lip/Sil}}$
$D_{\mathrm{Lip/Sil}}$	Lipid/silicone distribution ratio
$C_{\mathrm{Eel,lip}}$	Lipid-normalized concentration in eel
$C_{\mathrm{Sed,OC}}$	Organic carbon-normalized concentration in sediment
$C_{\mathrm{Sed,free}}$	Freely dissolved concentration in the sediment interstitial porewater: i) $C_{\mathrm{Sed,free}} = C_{\mathrm{Sil,sed}} / K_{\mathrm{Sil/W}}$ ii) $C_{\mathrm{Sed,free}} = C_{\mathrm{Sed,OC}} / (0.35 * K_{\mathrm{OW}})^{1}$ $C_{\mathrm{Sed,free}} = C_{\mathrm{Sed,OC}} / (0.63 * K_{\mathrm{OW}})^{2}$ $C_{\mathrm{Sed,free}} = C_{\mathrm{Sed,OC}} / (0.98 * K_{\mathrm{OW}})^{3}$
K_{OC}	Organic carbon/water partition ratio
$K_{\mathrm{Lip/OC}}$	Lipid/OC partition ratio
a_{Eel}	Chemical activity in eel
a_{Sed}	Chemical activity in sediment

References

(1) Seth, R.; Mackay, D.; Muncke, J. *Environ. Sci. Technol*. **1999**, 33, 2390-2394.

(2) Karickhoff, S.W.; Brown, D.S.; Scott, T.A. *Water Res.* **1979**, 13, 241-248.

(3) Di Toro, D.M.; Zarba, C.S.; Hansen, D.J.; Berry, W.J.; Swartz, R.C.; Cowan, C.E.; Pavlou, S.P.; Allen, H.E.; Thomas N.A.; Paquin, P.R. *Environ. Toxicol. Chem*. **1991**, 10, 1541-1583.

Table S2. Concentrations of the model chemicals in SSP-M823 thin-films equilibrated with intact eel tissue [$C_{\text{Sil,eel}}$, pg/g silicone], average ± standard deviations.

	HCB	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 118**	**PCB 153**	**PCB 138**	**PCB 180**
Eel A	n.q.	<54	94 ± 16	306 ± 51	809 ± 109	2620 ± 320	1960 ± 300	1260 ± 200
Eel B	130 [a]	<54	102 ± 8 [b]	237 ± 5 [b]	832 ± 48 [b]	1990 ± 20 [b]	1680 ± 50 [b]	837 ± 14 [b]
Eel C	207 ± 10 [b]	<54	76 ± 2	141 ± 8	736 ± 24	2400 ± 90	1720 ± 80	1090 ± 70
Eel D	322 ± 38	<54	115 ± 6	274 ± 13	1100 ± 50	2350 ± 50	1850 ± 60	850 ± 31
Eel E	268 [a]	<54	48 ± 2	69 ± 3	432 ± 7	1470 ± 50	699 ± 22	723 ± 26
Average	254 ± 78	<54	86 ± 25	203 ± 96	778 ± 235	2180 ± 450	1570 ± 500	959 ± 220

n.q. Not quantified due to chromatographic interference.

[a] Single value.

[b] Mean of duplicates with absolute deviation.

Table S3. Concentrations of the model chemicals in DC1-2577 coatings of glass jars equilibrated with sediment [$C_{\mathrm{Sil,sed}}$, ng/g silicone], average ± standard deviations. All quantifiable data points were included.

Location	**HCB**	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 118**	**PCB 153**	**PCB 138**	**PCB 180**
#4 2011[a]	<12.5	1.15 ± 0.03[b]	1.36 ± 0.18[b]	6.83 ± 0.38	4.15 ± 0.22	18.6 ± 1.1	24.5 ± 1.3	11.5 ± 1.3
#1 2012[c]	<0.77	2.24 ± 0.15[d]	4.15 ± 0.26	16.5 ± 2.0	7.99 ± 1.09	35.7 ± 4.2	46.7 ± 5.6	23.1 ± 2.1
#2 2012[c]	<0.77	2.59 ± 0.42	6.38 ± 1.42	19.2 ± 3.2	5.40 ± 0.70	33.9 ± 5.8	40.9 ± 7.0	26.4 ± 4.3
#3 2012[c]	<0.77	2.61 ± 0.33	5.53 ± 0.95	22.3 ± 3.3	10.5 ± 1.3	44.6 ± 7.8	60.3 ± 9.2	29.7 ± 6.2
#4 2012[c]	1.01[e]	<2.07	<2.86	8.47 ± 1.34	5.11 ± 0.85	22.2 ± 3.4	29.7 ± 4.2	14.3 ± 0.7
#5 2012[c]	<0.77	2.87 ± 0.52	5.12 ± 0.03	20.1 ± 1.1	9.01 ± 0.51	41.6 ± 2.6	54.7 ± 1.5	27.9 ± 1.8
Average 2012	1.01[e]	2.61 ± 0.40	5.30 ± 1.12	17.3 ± 5.4	7.60 ± 2.29	35.6 ± 9.1	46.4 ± 12.2	24.3 ± 6.4
Overall average 2011/12	1.01[e]	2.29 ± 0.71	4.51 ± 1.91	13.4 ± 6.7	6.31 ± 2.47	29.2 ± 11.0	38.2 ± 14.4	19.5 ± 8.1

[a] Data from glass jars with 2 µm, 4 µm and 8 µm coatings (n_{total} = 9).
[b] Data from the glass jars with 8 µm silicone coatings only (n = 3).
[c] Data from glass jars with 1 µm, 2 µm and 4 µm coatings (n_{total} = 3).
[d] Average of two data points ± absolute deviation.
[e] Single value.
n.q. Not quantified due to chromatographic interference.
n.a. Not available.

Table S4. Equilibrium partitioning concentrations of the model chemicals in eel lipids [$C_{\text{Lip,eq}}$, ng/g lipid] calculated as $C_{\text{Sil,eel}}$ times the compound-specific lipid/silicone distribution ratio ($D_{\text{Lip/Sil}}$[1]), average of triplicates ± standard deviations.

	HCB	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180
Eel A	n.q.	<0.87	1.50 ± 0.25	6.34 ± 1.05	21.0 ± 2.8	71.7 ± 8.7	50.0 ± 7.6	40.4 ± 6.1
Eel B	1.75 [a]	<0.87	1.64 ± 0.13 [b]	4.91 ± 0.10 [b]	21.6 ± 1.3 [b]	54.5 ± 0.6 [b]	42.7 ± 1.2 [b]	26.9 ± 0.4 [b]
Eel C	2.80 ± 0.14 [b]	<0.87	1.22 ± 0.03	2.91 ± 0.16	19.1 ± 0.6	65.7 ± 2.4	43.8 ± 2.0	35.0 ± 2.1
Eel D	4.34 ± 0.51	<0.87	1.83 ± 0.10	5.68 ± 0.28	28.6 ± 1.3	64.4 ± 1.4	47.3 ± 1.4	27.4 ± 1.0
Eel E	3.62 [a]	<0.87	0.77 ± 0.03	1.43 ± 0.07	11.2 ± 0.2	40.1 ± 1.3	17.8 ± 0.6	23.3 ± 0.8
Average	3.43 ± 1.06	<0.87	1.37 ± 0.40	4.21 ± 1.99	20.2 ± 6.1	59.6 ± 12.3	40.1 ± 12.8	30.9 ± 7.1

n.q. Not quantified due to chromatographic interference.

[a] Single value.
[b] Mean of duplicates with absolute deviation.

Reference

(1) Jahnke, A.; McLachlan, M.S.; Mayer, P. *Chemosphere* **2008**, 73, 1575-1581.

Table S5. Lipid-normalized concentrations of the model chemicals in eel tissue from exhaustive extraction [$C_{\mathrm{Eel,lip}}$, ng/g lipid], average ± standard deviations of triplicates.

	HCB	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180
Eel A	<254	4.12[a]	2.83 ± 1.17	15.4 ± 9.2	31.5 ± 5.0	118 ± 13	86.8 ± 13.8	61.6 ± 10.6
Eel B	<254	2.03 ± 0.53[b]	2.45 ± 0.54	8.43 ± 2.69	25.5 ± 2.1	70.7 ± 7.5	58.0 ± 7.8	32.7 ± 4.1
Eel C	<254	<1.61	1.55 ± 0.10	3.95 ± 0.39	24.7 ± 1.7	92.8 ± 6.5	64.0 ± 3.1	45.4 ± 3.0
Eel D	<254	<1.61	2.10 ± 0.09	6.85 ± 0.33	32.9 ± 2.7	81.7 ± 4.2	62.5 ± 3.9	31.6 ± 2.4
Eel E	<254	<1.61	<1.38	2.31 ± 0.19	14.2 ± 1.5	59.3 ± 6.5	27.9 ± 2.7	31.3 ± 3.2
Average	n.a.	2.72 ± 1.26[c]	2.23 ± 0.74 [c]	7.39 ± 5.94	25.8 ± 7.3	84.6 ± 22.0	59.9 ± 20.5	40.5 ± 13.1

[a] Single value.
[b] Average of two data points with absolute deviation.
[c] Average and standard deviation of all quantifiable data points.
n.a. Not analyzed.

Table S6. Freely dissolved concentrations of the model chemicals in the interstitial pore water [$C_{Sed,free}$, pg/L] of the sediment from station #4 obtained by two different methods: i) calculated as the average of all quantifiable $C_{Sil,sed}$ divided by silicone/water partition ratios ($K_{Sil/W}$[1]) at 20 °C and extrapolated to the actual water temperature (6 °C): ii) calculated from $C_{Sed,OC}$ divided by K_{OC} (estimated as [0.35 * K_{OW}[2]][3], [0.63 * K_{OW}][4] or [0.98 * K_{OW}][5]). $C_{Sed,OC}$ for PCBs 28 and 52 was <MQL; hence the corresponding $C_{Sed,free}$ is given in parentheses and should be considered semi-quantitative.

Passive sampling approach [$C_{Sed,free} = C_{Sil,sed} / K_{Sil/W}$]								
	HCB	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 118**	**PCB 153**	**PCB 138**	**PCB 180**
20 °C	4.7[a]	1.6 ± 0.1	1.0 ± 0.2	1.8 ± 0.2	0.7 ± 0.1	1.7 ± 0.2	1.7 ± 0.2	0.5 ± 0.1
6 °C	n.a.	0.9 ± 0.1	0.6 ± 0.1	1.2 ± 0.2	0.4 ± 0.1	1.0 ± 0.1	1.1 ± 0.1	0.3 ± 0.04
Exhaustive extraction [$C_{Sed,free} = C_{Sed,OC} / K_{OC}$]								
	HCB	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 118**	**PCB 153**	**PCB 138**	**PCB 180**
20 °C, *Seth et al.*[3]	n.a.	(6.2 ± 0.9)	(1.7 ± 0.2)	2.9 ± 0.001	1.2 ± 0.1	2.3 ±0.2	1.4 ± 0.1	0.8 ± 0.1
20 °C, *Karickhoff et al.*[4]	n.a.	(3.5 ± 0.5)	(1.0 ± 0.1)	1.6 ± 0.001	0.7 ± 0.1	1.3 ±0.1	0.8 ± 0.1	0.5 ± 0.04
20 °C, *Di Toro et al.*[5]	n.a.	(2.2 ± 0.3)	(0.6 ± 0.1)	1.0 ± 0.001	0.4 ± 0.04	0.8 ±0.1	0.5 ± 0.04	0.3 ± 0.03

[a] single value.
n.a. not available.

References

(1) Smedes, F.; Geertsma, R.W.; van der Zande, T.; Booij, K. *Environ. Sci. Technol*. **2009**, 43, 7047-7054.

(2) Schenker, U.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. *Environ. Sci. Technol*. **2005**, 39, 8434-8441.

(3) Seth, R.; Mackay, D.; Muncke, J. *Environ. Sci. Technol*. **1999**, 33, 2390-2394.

(4) Karickhoff, S.W.; Brown, D.S.; Scott, T.A. *Water Res*. **1979**, 13, 241-248.

(5) Di Toro, D.M.; Zarba, C.S.; Hansen, D.J.; Berry, W.J.; Swartz, R.C.; Cowan, C.E.; Pavlou, S.P.; Allen, H.E.; Thomas N.A.; Paquin, P.R. *Environ. Toxicol. Chem*. **1991**, 10, 1541-1583.