Supporting information for

Predicting dissolved organic carbon partition and distribution coefficients of neutral and ionizable organic chemicals

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Table of content

S1. Linear regressions for predicting Log K_{DOC} from literature

Table S1.1. Linear regressions for predicting Log K_{DOC} (Log K_{DOC} = a Log K_{OW} + b) from literature.

n	Equation	Chemical	r	R^2	Log Kow range	DOC source	Method	Reference
1	Log K_{DOC} = 0.82 Log Kow + 0.19	Various	0.96	-	2.5-6	Aldrich HA	Various	Chin *et al.*, 1990
2	Log K_{DOC} = 0.24 Log Kow + 2.78	Various	0.61	-	4.53-6.04	Surface water	RP	Eadie *et al.*, 1990
3	Log K_{DOC} = 0.43 Log Kow + 1.58	Various	0.72	-	5.18-6.05	Surface water	RP	Eadie *et al.*, 1990
4	Log K_{DOC} = 0.85 Log Kow + 0.13	PCBs		0.99	4.53-7.73	Commercial HA	ED	Merkelbach *et al.*, 1993
5	Log K_{DOC} = 0.96 Log Kow - 0.51	Chlorinated pesticides		0.76	5.52-6.36	Commercial HA	SE	Ding and Wu, 1995
6	Log K_{DOC} = 0.93 Log Kow - 0.35	PAHs; PCBs; *p p′* DDT		0.81	3.92-6.50	Aldrich HA	RP	Ozretich *et al.*, 1995
7	Log K_{DOC} = 0.91 Log Kow - 0.75	PAHs; PCBs; *p p′* DDT		0.78	3.92-6.51	Surface water	RP	Ozretich *et al.*, 1995
8	Log K_{DOC} = 0.67 Log Kow + 1.46	Various		0.80	4.35-5.89	Aldrich HA	PS	Freidig *et al.*, 1998
9	Log K_{DOC} = 0.85 Log Kow + 0.27	Various	0.77	-	3.2-8	Aldrich HA	Various	Burkhard, 2000
10	Log K_{DOC} = 0.88 Log Kow - 0.11	Various	0.29	-	4.2-7	Natural HA and FA	Various	Burkhard, 2000
11	Log K_{DOC} = 0.99 Log Kow - 0.88	Various	0.64	-	3.2-7.4	Sediment	Various	Burkhard, 2000
12	Log K_{DOC} = 0.91 Log Kow - 0.22	Various	0.31	-	4.4-6.2	Soil	Various	Burkhard, 2000
13	Log K_{DOC} = 0.97 Log Kow - 1.27	Various	0.32	-	3.2-7	Surface water	Various	Burkhard, 2000
14	Log K_{DOC} = 0.85 Log Kow - 0.11	Various	0.78	-	-	Various	Various	Burkhard, 2000
15	Log K_{DOC} = 0.85 Log Kow - 0.25	Various	0.67	-	-	Natural DOC	Various	Burkhard, 2000
16	Log K_{DOC} = 0.71 Log Kow - 0.5	PCBs	0.69	-	-	Natural DOC	Various	Burkhard, 2000
17	Log K_{DOC} = 1.18 Log Kow - 1.56	PAHs	0.76	-	-	Natural DOC	Various	Burkhard, 2000
18	Log K_{DOC} = 0.77 Log Kow + 1.39	PAHs	0.95	0.91	2-7	Commercial HA	RP	Krop *et al.*, 2001
19	Log K_{DOC} = 1.2 Log Kow - 1	PAHs	0.95	0.91	3.4-6	Commercial HA	ED	Krop *et al.*, 2001
20	Log K_{DOC} = 1.06 Log Kow - 0.74	PAHs	0.94	0.88	3.9-6.5	Commercial HA	RP	Krop *et al.*, 2001
21	Log K_{DOC} = 0.88 Log Kow + 0.6	PAHs	0.96	0.93	4.5-6.3	Commercial HA	FQ	Krop *et al.*, 2001
22	Log K_{DOC} = 0.83 Log Kow + 0.02	Chlorinated chemicals	0.96	0.92	3.2-7.8	Commercial HA	ED	Krop *et al.*, 2001
23	Log K_{DOC} = 0.38 Log Kow + 2.8	Chlorinated chemicals	0.91	0.83	3.7-7	Commercial HA	SE	Krop *et al.*, 2001
24	Log KDOC = 1.11 Log Kow - 2	Chlorinated chemicals	0.91	0.82	6-7.8	Commercial HA	RP	Krop *et al.*, 2001
25	Log K_{DOC} = 0.47 Log Kow + 2.1	Various	-	0.40	0.2-8	Various	Various	Krop *et al.*, 2001
26	Log K_{DOC} = 0.68 Log Kow + 1.4	Various	-	0.65	3-7.5	Commercial HA	ED + FQ	Krop *et al.*, 2001
27	Log K_{DOC} = 0.66 Log Kow + 1.3	Various	-	0.57	4.5-7.5	Sediment HA	ED + FQ	Krop *et al.*, 2001
28	Log K_{DOC} = 0.53 Log Kow + 1.9	Various	-	0.34	3.3-7.5	Soil HA	ED + FQ	Krop *et al.*, 2001
29	Log K_{DOC} = 0.34 Log Kow + 2.9	Various	-	0.33	4.5-7.5	Water HA	ED + FQ	Krop *et al.*, 2001
30	Log K_{DOC} = 0.23 Log Kow + 3.4	Various	-	0.18	3.7-8	Natural FA	ED + FQ + RP	Krop *et al.*, 2001
31	Log K_{DOC} = 0.46 Log Kow + 2.3	Various	-	0.37	3.2-8	Natural HA	ED + FQ + RP	Krop *et al.*, 2001

32	Log K_{DOM} = 0.98 Log Kow - 0.39	PAHs	-	0.99	3.30-5.50	Commercial HA	PS	Poerschmann and Kopinke, 2001
33	Log K_{DOM} = 0.93 Log Kow - 0.54	PCBs	-	0.99	4.53-7.16	Commercial HA	PS	Poerschmann and Kopinke, 2001
34	Log K_{DOM} = 0.87 Log Kow - 0.64	Alkanes	-	0.99	4.51-7.57	Commercial HA	PS	Poerschmann and Kopinke, 2001
35	Log K_{DOC} = 0.99 Log Kow - 0.64	PCDD, PCDF	-	0.89	5.6-7.2	Aldrich HA	SE	Kim *et al.*, 2002
36	Log K_{DOC} = 0.81 Log Kow + 0.23	Various	-	0.43	3.7-6.5	HA	Various	Mott, 2002
37	Log K_{DOC} = 0.91 Log Kow - 0.78	Various	-	0.47	3.7-6.5	FA	Various	Mott, 2002
38	Log K_{DOC} = 0.22 Log Kow + 3.46	Various	-	0.10	3.41-6.5	Various	Various	Mott, 2002
39	Log K_{DOC} = 0.77 Log Kow + 1.34	PCDDs, PCDFs, PCBs	0.84	-	7.0-8.0	Soil	SE	Fukushima *et al.*, 2006
40	Log K_{DOC} = 1.23 Log Kow - 0.91	PAHs	-	0.99	5.0-7.0	Aldrich HA	PS	ter Laak *et al.*, 2005
41	Log K_{DOC} = 0.76 Log Kow + 1.54	PCBs	-	0.94	5.5-7.4	Aldrich HA	PS	Durjava *et al.*, 2007
42	Log K_{DOC} = 0.86 Log Kow - 0.98	PAHs; PCBs	-	0.77	5.5-7.5	Aldrich HA	PS	Durjava *et al.*, 2007
43	Log K_{DOC} = 1.31 Log Kow - 1.86	PAHs	-	0.97	4.57-6.12	Sediment	PS	Haftka *et al.*, 2010
44	Log K_{DOC} = 1.18 Log Kow - 0.61	PAHs	-	0.98	4.57-6.12	Sediment	PS	Haftka *et al.*, 2010
45	Log K_{DOC} = 0.62 Log Kow + 0.98	Various	-	0.98	2.5-7.5	Soil	PS	Haftka *et al.*, 2013
46	Log K_{DOC} = 0.79 Log Kow + 1.28	PCBs	-	0.47	4.4-8.3	Sediment	PS	Kupryianchyk *et al.*, 2013
47	Log K_{DOC} = 0.91 Log Kow	PAHs	-	0.85	3.30-5.50	Aldrich HA	PS	de Perre *et al.*, 2014
48	Log K_{DOC} = 1.10 Log Kow	PAHs	-	0.97	3.30-5.50	Aldrich HA	PS	de Perre *et al.*, 2014
49	Log K_{DOC} = 0.76 Log Kow + 1.04	Various	-	0.85	3.7-5.7	Surface water	PS	Ripszam and Haglund, 2015
50	Log K_{DOC} = 0.96 Log Kow + 0.55	PAHs	-	0.93	3.40-6.63	Soil	PS	Enell *et al.*, 2016
51	Log K_{DOC} = 1.10 Log Kow + 0.31	O- and N – PACs	-	0.82	2.11-5.31	Soil	PS	Enell *et al.*, 2016
52	Log K_{DOC} = 0.89 Log Kow + 1.03	PACs	-	0.89	2.11-6.63	Soil	PS	Enell *et al.*, 2016

ED: equilibrium dialysis. FQ: fluorescence quenching. RP: reverse phase. SE: solubility enchantment. PS: passive sampling. PAHs: polycyclic aromatic hydrocarbons. PCBs: polychlorinated biphenyls. PCDDs: polychlorinated dibenzo-p-dioxins. PCDFs: polychlorinated dibenzofurans. PACs: polycyclic aromatic compounds.

S2. LSER descriptors and chemical properties of the target contaminants

Table S2.1. LSER descriptors, Log K_{OW} and acid (A-Pka) and base (B-Pka) dissociation constants of the target chemicals.

Record number	Chemical	CAS	E[1]	S[1]	A[1]	B[1]	V[1]	Log K_{OW}[2]	A-Pka[2]	B-Pka[2]	Chemical type
1	4-Chloro-3,5-dimethylphenol	88-04-0	0.98	0.94	0.61	0.26	1.179	3.38	9.76	-	Acid
2	Oxybenzone	131-57-7	1.65	1.63	0	0.62	1.739	4	7.56	-	Acid
3	Estradiol	50-28-2	1.8	1.77	0.86	1.1	2.199	4.15	10.27	-	Acid
4	3-Methoxyphenol	150-19-6	0.88	1.17	0.59	0.39	0.975	1.82	9.59	-	Acid
5	Nonylphenol	104-40-5	0.77	0.88	0.55	0.36	2.04	6.14	10.15		Acid
6	4-Methylphenol	106-44-5	0.82	0.87	0.57	0.31	0.92	2.07	10.21	-	Acid
7	4-Chlorophenol	106-48-9	0.92	1.08	0.67	0.20	0.90	2.42	9.47	-	Acid
8	3-Chlorophenol	108-43-0	0.91	1.06	0.69	0.15	0.90	2.35	9	-	Acid
9	4-Bromophenol	106-41-2	1.08	1.17	0.67	0.19	0.95	2.58	9.34	-	Acid
10	2,4,6-Trimethylphenol	527-60-6	0.86	0.81	0.30	0.45	1.20	2.94	10.97	-	Acid
11	2,6-Dichlorophenol	87-65-0	0.90	0.86	0.36	0.24	1.02	2.9	7.02	-	Acid
12	2,5-Dichlorophenol	583-78-8	0.96	0.84	0.52	0.18	1.02	3.02	7.53	-	Acid
13	4-Chloro-3-methylphenol	59-50-7	0.92	0.99	0.67	0.22	1.04	2.89	9.63	-	Acid
14	Bisphenol A	80-05-7	1.61	1.49	1.01	0.91	1.86	3.64	10.29	-	Acid
15	3,4-Dichlorophenol	95-77-2	1.02	1.24	0.93	0.00	1.02	3.16	8.56	-	Acid
16	3,5-Dichlorophenol	591-35-5	1.02	1.02	0.92	0.00	1.02	3.16	8.04	-	Acid
17	2,4,6-Trichlorophenol	88-06-2	1.01	0.80	0.60	0.15	1.14	3.77	6.59	-	Acid
18	2,3,6-Trichlorophenol	933-75-5	1.01	0.88	0.62	0.15	1.14	3.64	6.06	-	Acid
19	2,3,4,6-Tetrachlorophenol	58-90-2	1.10	0.87	0.50	0.15	1.26	4.44	5.63	-	Acid
20	Triclosan	3380-34-5	1.73	1.55	0.47	0.45	1.81	5.34	7.8	-	Acid
21	Pentachlorophenol	87-86-5	1.22	0.91	0.66	0.06	1.39	5.12	4.68	-	Acid
22	2,4-Dichlorophenol	120-83-2	0.96	0.82	0.54	0.17	1.02	3.1	8.05	-	Acid
23	2,4-Dimethylphenol	105-67-9	0.84	0.79	0.52	0.40	1.06	2.5	10.61	-	Acid
24	4-Fluorophenol	371-41-5	0.67	0.97	0.63	0.23	0.79	1.84	9.92	-	Acid
25	4-Iodophenol	540-38-5	1.38	1.22	0.68	0.20	1.03	2.99	9.3	-	Acid
26	Triclabendazole	68786-66-3	3.07	1.68	0.37	1.07	2.24	5.44	7.97	3.65	Amphoteric
27	Diflufenican	83164-33-4	2.4	1.06	0.26	1.3	2.435	4.94	9.03	0.63	Amphoteric
28	Carbamazepine	298-46-4	2.15	1.90	0.50	1.15	1.81	1.9	13.94	-	Amphoteric
29	Acridine	260-94-6	2.36	1.32	0.00	0.58	1.41	3.45	-	5.56	Base
30	4-Bromoaniline	106-40-1	1.19	1.19	0.31	0.30	0.99	2.28	-	3.9	Base
31	Alachlor	15972-60-8	1.16	1.20	0.00	1.15	2.14	3.05	-	1.2	Base
32	Terbutryn	886-50-0	1.43	1.23	0.12	0.99	1.94	3.38	-	4.03	Base
33	Diazinon	333-41-5	1.04	1.01	0.00	1.19	2.31	3.44	-	1.21	Base
34	Pirimiphos methyl	29232-93-7	1.78	1.52	0.31	2.05	2.09	6.62	-	3.74	Base
35	2,4-Dibromoaniline	615-57-6	1.37	1.19	0.27	0.29	1.17	3.52	-	1.83	Base
36	Irgarol	28159-98-0	1.69	1.39	0.26	1.08	1.97	3.26	-	4.13	Base
37	Chlorpromazine	50-53-3	2.16	1.57	0.00	1.01	2.41	5.18	-	9.41	Base
38	Triflupromazine	146-54-3	1.66	1.37	0.00	1.00	2.48	5.16	-	9.4	Base
39	Clotrimazol	23593-75-1	2.55	2.60	0.00	1.21	2.62	4.92	-	6.12	Base
40	Promazine	58-40-2	2.05	1.49	0.00	1.08	2.28	4.69	-	9.43	Base
41	Bromophos methyl	2104-96-3	1.51	1.51	0.00	0.46	1.96	5.17	-	-	Neutral
42	Cyfluthrin	68359-37-5	1.51	2.52	0.05	1.13	3.01	6.42	-	-	Neutral
43	Deltamethrin	52918-63-5	1.98	2.80	0.05	1.11	3.08	6.42	-	-	Neutral
44	Cypermethrin	52315-07-8	2.05	1.94	0.00	1.15	2.97	6.41	-	-	Neutral

45	trans-permethrin	61949-77-7	1.95	1.88	0.00	0.98	2.82	7.64	-	-	Neutral
46	2-Methylanthracenedione	84-54-8	1.41	1.48	0.00	0.56	1.67	3.81	-	-	Neutral
47	7H-Benz(de)anthracen-7-one	82-05-3	2.47	1.80	0.00	0.45	1.74	4.67	-	-	Neutral
48	9-Fluorenone	486-25-9	1.75	1.51	0.00	0.36	1.37	3.49	-	-	Neutral
49	Acenaphthylene	208-96-8	1.75	1.14	0.00	0.26	1.22	3.27	-	-	Neutral
50	Anthracene	120-12-7	2.29	1.34	0.00	0.28	1.45	4.54	-	-	Neutral
51	Anthracene-9,10-dione	84-65-1	1.41	1.45	0.00	0.55	1.53	3.06	-	-	Neutral
52	Benzo[a]anthracene	56-55-3	2.99	1.70	0.00	0.35	1.82	5.73	-	-	Neutral
53	Benzo[a]pyrene	50-32-8	3.63	1.96	0.00	0.37	1.95	6.19	-	-	Neutral
54	Benzo[b]fluoranthene	205-99-2	3.19	1.82	0.00	0.40	1.95	6.19	-	-	Neutral
55	Benzo[g,h,i]perylene	191-24-2	4.07	1.90	0.00	0.45	2.08	6.65	-	-	Neutral
56	Benzo[h]quinoline	230-27-3	1.88	1.22	0.00	0.48	1.41	3.31	-	-	Neutral
57	Benzo[k]fluoranthene	207-08-9	3.19	1.91	0.00	0.33	1.95	6.19	-	-	Neutral
58	Biphenyl	92-52-4	1.36	0.99	0.00	0.26	1.32	4.09	-	-	Neutral
59	Carbazole	86-74-8	1.79	1.82	0.22	0.18	1.32	3.76	-	-	Neutral
60	Chlorothalonil	1897-45-6	1.56	2.30	0.00	0.28	1.52	3.04	-	-	Neutral
61	Chlorpyrifos-methyl	5598-13-0	1.37	1.50	0.00	0.50	1.87	3.99	-	-	Neutral
62	Dibenzo[a,h]anthracene	53-70-3	4.00	2.04	0.00	0.44	2.19	6.91	-	-	Neutral
63	Dibutyl phthalate	84-74-2	0.70	1.27	0.00	0.95	2.27	4.75	-	-	Neutral
64	Ethoprophos	13194-48-4	0.67	0.53	0.00	0.84	1.88	3.39	-	-	Neutral
65	Fluorene	86-73-7	1.59	1.06	0.00	0.25	1.36	4.32	-	-	Neutral
66	Hexachlorobutadiene	87-68-3	1.02	0.42	0.00	0.16	1.32	4.91	-	-	Neutral
67	Indeno(cd)pyrene	193-39-5	3.61	1.93	0.00	0.42	2.08	6.65	-	-	Neutral
68	Methoxychlor	72-43-5	1.59	2.09	0.00	0.73	2.37	5.07	-	-	Neutral
69	Naphthalene	91-20-3	1.34	0.92	0.00	0.20	1.09	3.36	-	-	Neutral
70	Octocrylene	6197-30-4	1.59	2.03	0.05	0.80	3.06	6.89	-	-	Neutral
71	Pendimethalin	40487-42-1	1.39	1.39	0.16	0.71	2.15	5.2	-	-	Neutral
72	Pentachlorobenzene	608-93-5	1.33	0.92	0.06	0.00	1.33	5.22	-	-	Neutral
73	Phenanthrene	85-01-8	2.06	1.29	0.00	0.29	1.45	4.54	-	-	Neutral
74	Picoxystrobin	117428-22-5	1.28	1.94	0.00	1.27	2.47	3.47	-	-	Neutral
75	Pyrene	129-00-0	2.81	1.71	0.00	0.28	1.58	5	-	-	Neutral
76	Trifluralin	1582-09-8	0.99	1.72	0.00	0.60	2.20	4.56	-	-	Neutral
77	Testosterone	58-22-0	1.54	2.56	0.32	1.17	2.38	3.18	-	-	Neutral
78	Tributyl phosphate	126-73-8	-0.09	0.62	0.00	1.29	2.24	3.83	-	-	Neutral
79	Triphenyl phosphate	126-73-8	1.75	1.78	0.00	1.05	2.37	4.59	-	-	Neutral
80	PCB 14	34883-41-5	1.65	1.18	0.00	0.16	1.57	5.28	-	-	Neutral
81	PCB 18	37680-65-2	1.75	1.35	0.00	0.17	1.69	5.24	-	-	Neutral
82	PCB 28	7012-37-5	1.76	1.33	0.00	0.15	1.69	5.67[3]	-	-	Neutral
83	PCB 35	37680-69-6	1.80	1.31	0.00	0.13	1.69	5.82[3]	-	-	Neutral
84	PCB 52	35693-99-3	1.90	1.48	0.00	0.15	1.81	5.83	-	-	Neutral
85	PCB 72	41464-42-0	1.93	1.46	0.00	0.13	1.81	6.26[3]	-	-	Neutral
86	PCB 77	32598-13-3	1.94	1.44	0.00	0.11	1.81	6.5	-	-	Neutral
87	PCB 101	37680-73-2	2.04	1.61	0.00	0.13	1.94	6.44	-	-	Neutral
88	PCB 118	31508-00-6	2.06	1.59	0.00	0.11	1.94	6.77	-	-	Neutral
89	PCB 126	57465-28-8	2.11	1.57	0.00	0.09	1.94	7.03	-	-	Neutral
90	PCB 153	35065-27-1	2.18	1.74	0.00	0.11	2.06	7.04	-	-	Neutral
91	PCB 180	35065-29-3	2.29	1.87	0.00	0.09	2.18	7.51	-	-	Neutral
92	PCB 203	52663-76-0	2.48	2.00	0.00	0.06	2.30	7.65[3]	-	-	Neutral
93	PBDE 99	60348-60-9	2.71	1.59	0.00	0.07	2.26	7.31	-	-	Neutral
94	PBDE 153	446255-03-4	3.09	1.58	0.00	0.21	2.43	7.4[3]	-	-	Neutral
95	PBDE 183	207122-16-5	3.51	1.65	0.00	0.57	2.61	8.19	-	-	Neutral
96	cis-permethrin	54774-45-7	1.95	1.87	0	0.98	2.819	7.64	-	-	Neutral
97	Bifenthrin	82657-04-3	1.05	1.36	0	0.95	2.972	7.31	-	-	Neutral

98	2,4'-DDD	72-54-8	1.8	1.73	0.1	0.26	2.096	5.82	-	-	Neutral
99	Acenaphthene	83-32-9	1.6	1.05	0	0.22	1.259	3.73	-	-	Neutral
100	Chlorpyrifos	2921-88-2	1.59	0.92	0	1.01	2.15	5	-	-	Neutral
101	Chrysene	218-01-9	3.03	1.73	0	0.36	1.823	5.73	-	-	Neutral
102	Fluoranthene	206-44-0	2.38	1.55	0	0.24	1.585	5	-	-	Neutral
103	Hexachlorobenzene	118-74-1	1.49	0.75	0	0.09	1.451	5.75	-	-	Neutral
104	Metolachlor	51218-45-2	1.11	1.53	0	1.25	2.281	3.03	-	-	Neutral
105	Trans-chlorfenvinfos	470-90-6	1.21	1.56	0	0.99	2.325	4.52	-	-	Neutral

[1]UFZ-LSER database (Ulrich *et al.*, 2017). [2]ChEMBL database (2018), using predicted values by ACD software. [3]PubChem database (2018).

S3. Log K_{DOC}/D_{DOC} database

Table S3.1. Log K_{DOC} dataset. Log K_{DOC}/D_{DOC}, pH of the experiment.

Record number	Chemical	CAS	Log K_{DOC}/D_{DOC}	DOC source	pH	Reference
1	4-Methylphenol	106-44-5	2.11	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
2	4-Chlorophenol	106-48-9	2.31	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
3	3-Chlorophenol	108-43-0	2.46	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
4	4-Bromophenol	106-41-2	2.34	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
5	2,4,6-Trimethylphenol	527-60-6	2.29	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
6	2,6-Dichlorophenol	87-65-0	2.58	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
7	2,5-Dichlorophenol	583-78-8	2.58	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
8	4-Chloro-3-methylphenol	59-50-7	2.47	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
9	4-Chloro-3,5-dimethylphenol	88-04-0	2.83	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
10	3,4-Dichlorophenol	95-77-2	2.87	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
11	3,5-Dichlorophenol	591-35-5	2.84	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
12	2,4,6-Trichlorophenol	88-06-2	2.69	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
13	2,3,6-Trichlorophenol	933-75-5	2.72	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
14	2,3,4,6-Tetrachlorophenol	58-90-2	2.91	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
15	Pentachlorophenol	87-86-5	3.00	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
16	2,4-Dichlorophenol	120-83-2	2.50	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
17	2,4-Dimethylphenol	105-67-9	2.24	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
18	4-Fluorophenol	371-41-5	2.32	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
19	4-Iodophenol	540-38-5	2.69	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
20	3-Methoxyphenol	150-19-6	2.00	Aldrich HA	7.3	Ohlenbusch *et al.*, 2000
21	Bisphenol A	80-05-7	4.78	Acros HA[1]	6	Hu *et al.*, 2006
22	Bisphenol A	80-05-7	5.37	Acros HA[2]	6	Hu *et al.*, 2006
23	Bisphenol A	80-05-7	4.94	Acros HA[3]	6	Hu *et al.*, 2006
24	Bisphenol A	80-05-7	4.35	Acros HA[4]	6	Hu *et al.*, 2006
25	Bisphenol A	80-05-7	4.06	Acros HA[5]	6	Hu *et al.*, 2006
26	Bisphenol A	80-05-7	5.20	Acros HA[6]	7	Hu *et al.*, 2006
27	Bisphenol A	80-05-7	5.60	Acros HA[7]	7	Hu *et al.*, 2006
28	Bisphenol A	80-05-7	4.85	Acros HA[8]	7	Hu *et al.*, 2006
29	Bisphenol A	80-05-7	4.29	Acros HA[9]	7	Hu *et al.*, 2006
30	Bisphenol A	80-05-7	4.03	Acros HA[10]	7	Hu *et al.*, 2006
31	Bisphenol A	80-05-7	5.43	Acros HA[11]	7	Hu *et al.*, 2006
32	Bisphenol A	80-05-7	4.92	Acros HA[12]	7	Hu *et al.*, 2006
33	Bisphenol A	80-05-7	4.71	Acros HA[13]	7	Hu *et al.*, 2006
34	Bisphenol A	80-05-7	4.16	Acros HA[14]	7	Hu *et al.*, 2006
35	Bisphenol A	80-05-7	4.04	Acros HA[15]	7	Hu *et al.*, 2006
36	PCB 14	34883-41-5	4.63	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
37	PCB 18	37680-65-2	4.54	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009

38	PCB 28	7012-37-5	4.95	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
39	PCB 35	37680-69-6	5.2	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
40	PCB 52	35693-99-3	5.12	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
41	PCB 72	41464-42-0	5.37	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
42	PCB 77	32598-13-3	5.77	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
43	PCB 101	37680-73-2	5.6	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
44	PCB 118	31508-00-6	5.85	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
45	PCB 126	57465-28-8	6.39	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
46	PCB 153	35065-27-1	6.1	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
47	PCB 180	35065-29-3	6.39	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
48	PCB 203	52663-76-0	5.96	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
49	PBDE 99	60348-60-9	6.35	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
50	PBDE 153	446255-03-4	6.71	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
51	PBDE 183	207122-16-5	6.63	Aldrich HA	6.83-7.05	Ter Laak *et al.*, 2009
52	Cyfluthrin	68359-37-5	4.75	Soil porewater	6.3	Delgado-Moreno *et al.*, 2010
53	cis-permethrin	54774-45-7	4.84	Soil porewater	6.3	Delgado-Moreno *et al.*, 2010
54	trans-permethrin	61949-77-7	4.83	Soil porewater	6.3	Delgado-Moreno *et al.*, 2010
55	Bifenthrin	82657-04-3	4.68	Soil porewater	6.3	Delgado-Moreno *et al.*, 2010
56	Nonylphenol	104-40-5	3.25	Wastewater	7.8	Neale *et al.*, 2011
57	Carbamazepine	298-46-4	3.14	Wastewater	7.8	Neale *et al.*, 2011
58	Terbutryn	886-50-0	2.80	Wastewater	7.8	Neale *et al.*, 2011
59	Irgarol	28159-98-0	3.12	Wastewater	7.8	Neale *et al.*, 2011
60	Benzo[a]pyrene	50-32-8	3.75	Wastewater	7.8	Neale *et al.*, 2011
61	Chlorpyrifos	2921-88-2	3.12	Wastewater	7.8	Neale *et al.*, 2011
62	Dibenzo[ah]anthracene	53-70-3	4.05	Wastewater	7.8	Neale *et al.*, 2011
63	Methoxychlor	72-43-5	3.06	Wastewater	7.8	Neale *et al.*, 2011
64	Metolachlor	51218-45-2	2.86	Wastewater	7.8	Neale *et al.*, 2011
65	Pyrene	129-00-0	3.16	Wastewater	7.8	Neale *et al.*, 2011
66	Oxybenzone	131-57-7	3.33	Soil porewater	5.38	Haftka *et al.*, 2013
67	Estradiol	50-28-2	3.23	Soil porewater	5.38	Haftka *et al.*, 2013
68	Triclosan	3380-34-5	3.89	Soil porewater	5.38	Haftka *et al.*, 2013
69	Triclabendazole	68786-66-3	4.89	Soil porewater	5.38	Haftka *et al.*, 2013
70	Testosterone	58-22-0	3.18	Soil porewater	5.38	Haftka *et al.*, 2013
71	Bromophos methyl a	2104-96-3	3.98	Soil porewater	5.38	Haftka *et al.*, 2013
72	Deltamethrin	52918-63-5	5.23	Soil porewater	5.38	Haftka *et al.*, 2013
73	cis-Permethrin	54774-45-7	5.62	Soil porewater	5.38	Haftka *et al.*, 2013
74	Cypermethrin	52315-07-8	5.2	Soil porewater	5.38	Haftka *et al.*, 2013
75	trans-Permethrin	61949-77-7	5.62	Soil porewater	5.38	Haftka *et al.*, 2013
76	octocrylene	6197-30-4	5.52	Soil porewater	5.38	Haftka *et al.*, 2013
77	Chlorpromazine	50-53-3	4.20	Soil porewater	5.38	Haftka *et al.*, 2013
78	Chlorpromazine	50-53-3	4.78	Soil porewater	5.38	Haftka *et al.*, 2013
79	Clotrimazol	23593-75-1	4.67	Soil porewater	5.38	Haftka *et al.*, 2013
80	Clotrimazol	23593-75-1	4.64	Soil porewater	5.38	Haftka *et al.*, 2013
81	Triflupromazine	146-54-3	3.90	Soil porewater	5.38	Haftka *et al.*, 2013

82	Triflupromazine	146-54-3	4.55	Soil porewater	5.38	Haftka *et al.*, 2013
83	Triclosan	3380-34-5	3.84	Surface water	4.7	Haftka *et al.*, 2013
84	Triclabendazole	68786-66-3	5.27	Surface water	4.7	Haftka *et al.*, 2013
85	Triclabendazole	68786-66-3	5.12	Surface water	5.3	Haftka *et al.*, 2013
86	Triclabendazole	68786-66-3	4.48	Surface water	7.13	Haftka *et al.*, 2013
87	Bromophos methyl a	2104-96-3	4.19	Surface water	4.7	Haftka *et al.*, 2013
88	Bromophos methyl a	2104-96-3	3.87	Surface water	7.13	Haftka *et al.*, 2013
89	Deltamethrin	52918-63-5	5.16	Surface water	6.94	Haftka *et al.*, 2013
90	Deltamethrin	52918-63-5	5.21	Surface water	7.13	Haftka *et al.*, 2013
91	cis-Permethrin	54774-45-7	5.73	Surface water	4.7	Haftka *et al.*, 2013
92	cis-Permethrin	54774-45-7	5.73	Surface water	7.13	Haftka *et al.*, 2013
93	Cypermethrin	52315-07-8	5.15	Surface water	7.13	Haftka *et al.*, 2013
94	trans-Permethrin	61949-77-7	5.72	Surface water	4.7	Haftka *et al.*, 2013
95	trans-Permethrin	61949-77-7	5.51	Surface water	6.94	Haftka *et al.*, 2013
96	trans-Permethrin	61949-77-7	5.6	Surface water	7.13	Haftka *et al.*, 2013
97	octocrylene	6197-30-4	5.64	Surface water	4.7	Haftka *et al.*, 2013
98	octocrylene	6197-30-4	4.78	Surface water	5.3	Haftka *et al.*, 2013
99	octocrylene	6197-30-4	4.99	Surface water	6.12	Haftka *et al.*, 2013
100	octocrylene	6197-30-4	5.23	Surface water	6.32	Haftka *et al.*, 2013
101	octocrylene	6197-30-4	5.55	Surface water	6.93	Haftka *et al.*, 2013
102	octocrylene	6197-30-4	5.02	Surface water	6.94	Haftka *et al.*, 2013
103	octocrylene	6197-30-4	5.15	Surface water	7.13	Haftka *et al.*, 2013
104	Clotrimazol	23593-75-1	4.76	Surface water	5.3	Haftka *et al.*, 2013
105	Chlorpromazine	50-53-3	4.50	Surface water	6.12	Haftka *et al.*, 2013
106	Chlorpromazine	50-53-3	4.02	Surface water	6.93	Haftka *et al.*, 2013
107	Chlorpromazine	50-53-3	4.46	Surface water	6.94	Haftka *et al.*, 2013
108	Chlorpromazine	50-53-3	4.04	Surface water	7.13	Haftka *et al.*, 2013
109	Clotrimazol	23593-75-1	4.27	Surface water	4.7	Haftka *et al.*, 2013
110	Clotrimazol	23593-75-1	5.02	Surface water	6.12	Haftka *et al.*, 2013
111	Clotrimazol	23593-75-1	5.14	Surface water	6.32	Haftka *et al.*, 2013
112	Clotrimazol	23593-75-1	4.19	Surface water	6.93	Haftka *et al.*, 2013
113	Clotrimazol	23593-75-1	4.36	Surface water	6.94	Haftka *et al.*, 2013
114	Clotrimazol	23593-75-1	4.64	Surface water	7.13	Haftka *et al.*, 2013
115	Promazine	58-40-2	3.61	Surface water	6.93	Haftka *et al.*, 2013
116	Promazine	58-40-2	4.07	Surface water	6.94	Haftka *et al.*, 2013
117	Promazine	58-40-2	3.61	Surface water	7.13	Haftka *et al.*, 2013
118	Triflupromazine	146-54-3	4.44	Surface water	4.7	Haftka *et al.*, 2013
119	Triflupromazine	146-54-3	4.70	Surface water	5.3	Haftka *et al.*, 2013
120	Triflupromazine	146-54-3	4.76	Surface water	6.12	Haftka *et al.*, 2013
121	Triflupromazine	146-54-3	4.43	Surface water	6.32	Haftka *et al.*, 2013
122	Triflupromazine	146-54-3	3.75	Surface water	6.93	Haftka *et al.*, 2013
123	Triflupromazine	146-54-3	4.14	Surface water	6.94	Haftka *et al.*, 2013
124	Triflupromazine	146-54-3	3.68	Surface water	7.13	Haftka *et al.*, 2013
125	Pirimiphos	29232-93-7	4.94	Surface water	7.8	Ripszam and Haglund, 2015

126	Diflufenican	83164-33-4	5.10	Surface water	7.8	Ripszan and Haglund, 2015
127	4-Bromoaniline	106-40-1	4.00	Surface water	7.8	Ripszan and Haglund, 2015
128	Alachlor	15972-60-8	4.01	Surface water	7.8	Ripszan and Haglund, 2015
129	Diazinon	333-41-5	4.97	Surface water	7.8	Ripszan and Haglund, 2015
130	2,4-Dibromoaniline	615-57-6	3.96	Surface water	7.8	Ripszan and Haglund, 2015
131	Tributyl phosphate	126-73-8	5.34	Surface water	7.8	Ripszan and Haglund, 2015
132	Triphenyl phosphate	126-73-8	4.98	Surface water	7.8	Ripszan and Haglund, 2015
133	2,4'-DDD	72-54-8	4.72	Surface water	7.8	Ripszan and Haglund, 2015
134	Anthracene	120-12-7	4.65	Surface water	7.8	Ripszan and Haglund, 2015
135	Biphenyl	92-52-4	3.74	Surface water	7.8	Ripszan and Haglund, 2015
136	Chlorothalonil	1897-45-6	4.73	Surface water	7.8	Ripszan and Haglund, 2015
137	Chlorpyrifos	2921-88-2	5.03	Surface water	7.8	Ripszan and Haglund, 2015
138	Chlorpyrifos-methyl	5598-13-0	4.59	Surface water	7.8	Ripszan and Haglund, 2015
139	Dibutyl phthalate	84-74-2	4.99	Surface water	7.8	Ripszan and Haglund, 2015
140	Ethoprophos	13194-48-4	4.63	Surface water	7.8	Ripszan and Haglund, 2015
141	Hexachlorobenzene	118-74-1	5.08	Surface water	7.8	Ripszan and Haglund, 2015
142	Hexachlorobutadiene	87-68-3	3.94	Surface water	7.8	Ripszan and Haglund, 2015
143	Metolachlor	51218-45-2	4.70	Surface water	7.8	Ripszan and Haglund, 2015
144	Naphthalene	91-20-3	4.21	Surface water	7.8	Ripszan and Haglund, 2015
145	Pendimethalin	40487-42-1	4.79	Surface water	7.8	Ripszan and Haglund, 2015
146	Pentachlorobenzene	608-93-5	4.68	Surface water	7.8	Ripszan and Haglund, 2015
147	Phenanthrene	85-01-8	4.32	Surface water	7.8	Ripszan and Haglund, 2015
148	Picoxystrobin	117428-22-5	4.92	Surface water	7.8	Ripszan and Haglund, 2015
149	Trans-chlorfenvinfos	470-90-6	4.82	Surface water	7.8	Ripszan and Haglund, 2015
150	Trifluralin	1582-09-8	4.75	Surface water	7.8	Ripszan and Haglund, 2015
151	Acridine	260-94-6	4.29	Soil porewater	4.7-8.63	Enell *et al.*, 2016
152	2-Methylanthracenedione	84-54-8	4.50	Soil porewater	4.7-8.63	Enell et *al.*, 2016
153	7H-Benz(de)anthracen-7-one	82-05-3	5.18	Soil porewater	4.7-8.63	Enell et *al.*, 2016
154	9-Fluorenone	486-25-9	3.84	Soil porewater	4.7-8.63	Enell et *al.*, 2016
155	Acenaphthene	83-32-9	4.25	Soil porewater	4.7-8.63	Enell et *al.*, 2016
156	Acenaphthylene	208-96-8	4.91	Soil porewater	4.7-8.63	Enell et *al.*, 2016
157	Anthracene	120-12-7	4.83	Soil porewater	4.7-8.63	Enell et *al.*, 2016
158	Anthracene-9,10-dione	84-65-1	4.24	Soil porewater	4.7-8.63	Enell et *al.*, 2016
159	Benzo[a]anthracene	56-55-3	5.68	Soil porewater	4.7-8.63	Enell et *al.*, 2016
160	Benzo[a]pyrene	50-32-8	6.49	Soil porewater	4.7-8.63	Enell et *al.*, 2016
161	Benzo[b]fluoranthene	205-99-2	6.22	Soil porewater	4.7-8.63	Enell et *al.*, 2016
162	Benzo[g,h,i]perylene	191-24-2	7.03	Soil porewater	4.7-8.63	Enell et *al.*, 2016
163	Benzo[h]quinoline	230-27-3	3.92	Soil porewater	4.7-8.63	Enell et *al.*, 2016
164	Benzo[k]fluoranthene	207-08-9	6.47	Soil porewater	4.7-8.63	Enell et *al.*, 2016
165	Carbazole	86-74-8	4.23	Soil porewater	4.7-8.63	Enell et *al.*, 2016
166	Chrysene	218-01-9	5.75	Soil porewater	4.7-8.63	Enell et *al.*, 2016
167	Dibenzo[a,h]anthracene	53-70-3	7.15	Soil porewater	4.7-8.63	Enell et *al.*, 2016
168	Fluoranthene	206-44-0	5.18	Soil porewater	4.7-8.63	Enell et *al.*, 2016
169	Fluorene	86-73-7	4.53	Soil porewater	4.7-8.63	Enell et *al.*, 2016

170	Indeno(cd)pyrene	193-39-5	7.02	Soil porewater	4.7-8.63	Enell et *al.*, 2016
171	Phenanthrene	85-01-8	4.59	Soil porewater	4.7-8.63	Enell et *al.*, 2016
172	Pyrene	129-00-0	5.12	Soil porewater	4.7-8.63	Enell et *al.*, 2016

[1] Acros HA (1 mg/L; 5 mM phosphate buffer). [2] Acros HA (2.5 mg/L; 5 mM phosphate buffer). [3] Acros HA (5 mg/L; 5 mM phosphate buffer). [4] Acros HA (25 mg/L; 5 mM phosphate buffer). [5] Acros HA 50 mg/L; 5 mM phosphate buffer). [6] Acros HA (1 mg/L; 5 mM phosphate buffer). [7] Acros HA (2.5 mg/L; 5 mM phosphate buffer). [8] Acros HA (5 mg/L; 5 mM phosphate buffer). [9] Acros HA (25 mg/L; 5 mM phosphate buffer). [10] Acros HA (50 mg/L; 5 mM phosphate buffer). [11] Acros HA (1 mg/L; 125 mM phosphate buffer). [12] Acros HA (2.5 mg/L; 125 mM phosphate buffer). [13] Acros HA (5 mg/L; 125 mM phosphate buffer). [14] Acros HA (25 mg/L; 125 mM phosphate buffer). [15] Acros HA (50 mg/L; 125 mM phosphate buffer).

S4. Training and validation datasets for organic neutral chemicals

Table S4.1. Dataset for LSER model for all DOC sources. LSER descriptors, Log K_{OW}, Log K_{DOC}.

Record number	Chemical	CAS	E^1	S^1	A^1	B^1	V^1	Log K_{OW}^{2}	Log K_{DOC}
Training dataset for all DOC									
1	Bromophos methyl	2104-96-3	1.51	1.51	0.00	0.46	1.96	5.17	4.01
2	Nonylphenol	104-40-5	0.77	0.88	0.55	0.36	2.04	6.14	3.25
3	Cyfluthrin	68359-37-5	1.51	2.52	0.05	1.13	3.01	6.42	4.75
4	Deltamethrin	52918-63-5	1.98	2.80	0.05	1.11	3.08	6.42	5.21
5	Cypermethrin	52315-07-8	2.05	1.94	0.00	1.15	2.97	6.41	5.18
6	trans-permethrin	61949-77-7	1.95	1.88	0.00	0.98	2.82	7.64	5.42
7	2-Methylanthracenedione	84-54-8	1.41	1.48	0.00	0.56	1.67	3.81	4.50
8	7H-Benz(de)anthracen-7-one	82-05-3	2.47	1.80	0.00	0.45	1.74	4.67	5.18
9	9-Fluorenone	486-25-9	1.75	1.51	0.00	0.36	1.37	3.49	3.84
10	Acenaphthylene	208-96-8	1.75	1.14	0.00	0.26	1.22	3.27	4.91
11	Acridine	260-94-6	2.36	1.32	0.00	0.58	1.41	3.45	4.29
12	Anthracene	120-12-7	2.29	1.34	0.00	0.28	1.45	4.54	4.74
13	Anthracene-9,10-dione	84-65-1	1.41	1.45	0.00	0.55	1.53	3.06	4.24
14	Benzo[a]anthracene	56-55-3	2.99	1.70	0.00	0.35	1.82	5.73	5.68
15	Benzo[a]pyrene	50-32-8	3.63	1.96	0.00	0.37	1.95	6.19	5.12
16	Benzo[b]fluoranthene	205-99-2	3.19	1.82	0.00	0.40	1.95	6.19	6.22
17	Benzo[g,h,i]perylene	191-24-2	4.07	1.90	0.00	0.45	2.08	6.65	7.03
18	Benzo[h]quinoline	230-27-3	1.88	1.22	0.00	0.48	1.41	3.31	3.92
19	Benzo[k]fluoranthene	207-08-9	3.19	1.91	0.00	0.33	1.95	6.19	6.47
20	Biphenyl	92-52-4	1.36	0.99	0.00	0.26	1.32	4.09	3.74
21	Carbazole	86-74-8	1.79	1.82	0.22	0.18	1.32	3.76	4.23
22	Chlorothalonil	1897-45-6	1.56	2.30	0.00	0.28	1.52	3.04	4.73
23	Chlorpyrifos-methyl	5598-13-0	1.37	1.50	0.00	0.50	1.87	3.99	4.59
24	Dibenzo[a,h]anthracene	53-70-3	4.00	2.04	0.00	0.44	2.19	6.91	5.60
25	Dibutyl phthalate	84-74-2	0.70	1.27	0.00	0.95	2.27	4.75	4.99
26	Ethoprophos	13194-48-4	0.67	0.53	0.00	0.84	1.88	3.39	4.63
27	Fluorene	86-73-7	1.59	1.06	0.00	0.25	1.36	4.32	4.53
28	Hexachlorobutadiene	87-68-3	1.02	0.42	0.00	0.16	1.32	4.91	3.94
29	Indeno(cd)pyrene	193-39-5	3.61	1.93	0.00	0.42	2.08	6.65	7.02
30	Methoxychlor	72-43-5	1.59	2.09	0.00	0.73	2.37	5.07	3.06
31	Naphthalene	91-20-3	1.34	0.92	0.00	0.20	1.09	3.36	4.21
32	octocrylene	6197-30-4	1.59	2.03	0.05	0.80	3.06	6.89	5.36
33	Pendimethalin	40487-42-1	1.39	1.39	0.16	0.71	2.15	5.20	4.79
34	Pentachlorobenzene	608-93-5	1.33	0.92	0.06	0.00	1.33	5.22	4.68
35	Phenanthrene	85-01-8	2.06	1.29	0.00	0.29	1.45	4.54	4.46
36	Picoxystrobin	117428-22-5	1.28	1.94	0.00	1.27	2.47	3.47	4.92

37	Pyrene	129-00-0	2.81	1.71	0.00	0.28	1.58	5.00	4.14
38	Trifluralin	1582-09-8	0.99	1.72	0.00	0.60	2.20	4.56	4.75
39	4-Methylphenol	106-44-5	0.82	0.87	0.57	0.31	0.92	2.07	2.11
40	4-Bromoaniline	106-40-1	1.19	1.19	0.31	0.30	0.99	2.28	4.00
41	4-Chlorophenol	106-48-9	0.92	1.08	0.67	0.20	0.90	2.42	2.31
42	Carbamazepine	298-46-4	2.15	1.90	0.50	1.15	1.81	1.90	3.14
43	3-Chlorophenol	108-43-0	0.91	1.06	0.69	0.15	0.90	2.35	2.46
44	4-Bromophenol	106-41-2	1.08	1.17	0.67	0.19	0.95	2.58	2.34
45	2,4,6-Trimethylphenol	527-60-6	0.86	0.81	0.30	0.45	1.20	2.94	2.29
46	4-Chloro-3-methylphenol	59-50-7	0.92	0.99	0.67	0.22	1.04	2.89	2.47
47	Bisphenol A	80-05-7	1.61	1.49	1.01	0.91	1.86	3.64	4.72
48	Testosterone	58-22-0	1.54	2.56	0.32	1.17	2.38	3.18	3.18
49	3,4-Dichlorophenol	95-77-2	1.02	1.24	0.93	0.00	1.02	3.16	2.87
50	Alachlor	15972-60-8	1.16	1.20	0.00	1.15	2.14	3.05	4.01
51	Terbutryn	886-50-0	1.43	1.23	0.12	0.99	1.94	3.38	2.80
52	Diazinon	333-41-5	1.04	1.01	0.00	1.19	2.31	3.44	4.97
53	Tributyl phosphate	126-73-8	-0.09	0.62	0.00	1.29	2.24	3.83	5.34
54	Triphenyl phosphate	126-73-8	1.75	1.78	0.00	1.05	2.37	4.59	4.98
55	Pirimiphos	29232-93-7	1.78	1.52	0.31	2.05	2.09	6.62	4.94
56	Triclosan	3380-34-5	1.73	1.55	0.47	0.45	1.81	5.34	3.87
57	2,4-Dibromoaniline	615-57-6	1.37	1.19	0.27	0.29	1.17	3.52	3.96
58	2,4-Dimethylphenol	105-67-9	0.84	0.79	0.52	0.40	1.06	2.5	10.61
59	4-Fluorophenol	371-41-5	0.67	0.97	0.63	0.23	0.79	1.84	2.32
60	4-Iodophenol	540-38-5	1.38	1.22	0.68	0.20	1.03	2.99	2.69
61	Irgarol	28159-98-0	1.69	1.39	0.26	1.08	1.97	3.26	3.12
62	Triclabendazole	68786-66-3	3.07	1.68	0.37	1.07	2.24	5.44	4.92
63	PCB 14	34883-41-5	1.65	1.18	0.00	0.16	1.57	5.28	4.63
64	PCB 28	7012-37-5	1.76	1.33	0.00	0.15	1.69	5.67	4.95
65	PCB 52	35693-99-3	1.90	1.48	0.00	0.15	1.81	5.83	5.12
66	PCB 77	32598-13-3	1.94	1.44	0.00	0.11	1.81	6.50	5.77
67	PCB 101	37680-73-2	2.04	1.61	0.00	0.13	1.94	6.44	5.60
68	PCB 180	35065-29-3	2.29	1.87	0.00	0.09	2.18	7.51	6.39
69	PCB 203	52663-76-0	2.48	2.00	0.00	0.06	2.30	7.65	5.96
70	PBDE 183	207122-16-5	3.51	1.65	0.00	0.57	2.61	8.19	6.63
71	PCB 72	41464-42-0	1.93	1.46	0.00	0.13	1.81	6.26	5.37
72	PCB 153	35065-27-1	2.18	1.74	0.00	0.11	2.06	6.92	6.10
73	PBDE 99	60348-60-9	2.71	1.59	0.00	0.07	2.26	7.31	6.35
Validation dataset for all DOC									
1	cis-permethrin	54774-45-7	1.95	1.87	0.00	0.98	2.82	7.64	5.48
2	Bifenthrin	82657-04-3	1.05	1.36	0.00	0.95	2.97	7.31	4.68
3	2,4'-DDD	72-54-8	1.80	1.73	0.10	0.26	2.10	5.82	4.72
4	Acenaphthene	83-32-9	1.60	1.05	0.00	0.22	1.26	3.73	4.25
5	Chlorpyrifos	2921-88-2	1.59	0.92	0.00	1.01	2.15	5.00	4.08
6	Chrysene	218-01-9	3.03	1.73	0.00	0.36	1.82	5.73	5.75

7	Diflufenican	83164-33-4	2.40	1.06	0.26	1.30	2.44	4.94	5.10
8	Fluoranthene	206-44-0	2.38	1.55	0.00	0.24	1.58	5.00	5.18
9	Hexachlorobenzene	118-74-1	1.49	0.75	0.00	0.09	1.45	5.75	5.08
10	Metolachlor	51218-45-2	1.11	1.53	0.00	1.25	2.28	3.03	3.78
11	Trans-chlorfenvinfos	470-90-6	1.21	1.56	0.00	0.99	2.33	4.52	4.82
12	4-Chloro-3,5-dimethylphenol	88-04-0	0.98	0.94	0.61	0.26	1.18	3.38	2.83
13	Oxybenzone	131-57-7	1.65	1.63	0.00	0.62	1.74	4.00	3.33
14	Estradiol	50-28-2	1.80	1.77	0.86	1.10	2.20	4.15	3.23
15	3-Methoxyphenol	150-19-6	0.88	1.17	0.59	0.39	0.97	1.82	2.00
16	PCB 18	37680-65-2	1.75	1.35	0.00	0.17	1.69	5.24	4.54
17	PCB 35	37680-69-6	1.80	1.31	0.00	0.13	1.69	5.82	5.20
18	PCB 118	31508-00-6	2.06	1.59	0.00	0.11	1.94	6.77	5.85
19	PCB 126	57465-28-8	2.11	1.57	0.00	0.09	1.94	7.03	6.39
20	PBDE 153	446255-03-4	3.09	1.58	0.00	0.21	2.43	7.40	6.71

[1] UFZ-LSER database (Ulrich *et al.*, 2017). [2] ChEMBL database (2018), using predicted values by ACD software.

Table S4.2. Dataset for LSER model for soil porewater DOC source. LSER descriptors, Log K_{OW}, Log K_{DOC}.

Record number	Chemical	CAS	E[1]	S[1]	A[1]	B[1]	V[1]	Log K_{OW}[2]	Log K_{DOC}
Training dataset for soil porewater									
1	Oxybenzone	131-57-7	1.65	1.63	0.00	0.62	1.74	4.00	3.33
2	Estradiol	50-28-2	1.80	1.77	0.86	1.10	2.20	4.15	3.23
3	Triclabendazole	68786-66-3	3.07	1.68	0.37	1.07	2.24	5.44	4.89
4	Acridine	260-94-6	2.36	1.32	0.00	0.58	1.41	3.45	4.29
5	Testosterone	58-22-0	1.54	2.56	0.32	1.17	2.38	3.18	3.18
6	Bromophos methyl a	2104-96-3	1.51	1.51	0.00	0.46	1.96	5.17	3.98
7	Deltamethrin	52918-63-5	1.98	2.80	0.05	1.11	3.08	6.42	5.23
8	cis-permethrin	54774-45-7	1.95	1.87	0.00	0.98	2.82	7.64	5.23
9	Cypermethrin	52315-07-8	2.05	1.94	0.00	1.15	2.97	6.41	5.20
10	trans-permethrin	61949-77-7	1.95	1.88	0.00	0.98	2.82	7.64	5.23
11	Bifenthrin	82657-04-3	1.05	1.36	0.00	0.95	2.97	7.31	4.68
12	2-Methylanthracenedione	84-54-8	1.41	1.48	0.00	0.56	1.67	3.81	4.50
13	7H-Benz(de)anthracen-7-one	82-05-3	2.47	1.80	0.00	0.45	1.74	4.67	5.18
14	Acenaphthene	83-32-9	1.60	1.05	0.00	0.22	1.26	3.73	4.25
15	Acenaphthylene	208-96-8	1.75	1.14	0.00	0.26	1.22	3.27	4.91
16	Anthracene	120-12-7	2.29	1.34	0.00	0.28	1.45	4.54	4.83
17	Anthracene-9,10-dione	84-65-1	1.41	1.45	0.00	0.55	1.53	3.06	4.24
18	Benzo[a]anthracene	56-55-3	2.99	1.70	0.00	0.35	1.82	5.73	5.68
19	Benzo[b]fluoranthene	205-99-2	3.19	1.82	0.00	0.40	1.95	6.19	6.22
20	Benzo[h]quinoline	230-27-3	1.88	1.22	0.00	0.48	1.41	3.31	3.92
21	Benzo[k]fluoranthene	207-08-9	3.19	1.91	0.00	0.33	1.95	6.19	6.47
22	Carbazole	86-74-8	1.79	1.82	0.22	0.18	1.32	3.76	4.23
23	Chrysene	218-01-9	3.03	1.73	0.00	0.36	1.82	5.73	5.75
24	Dibenzo[a,h]anthracene	53-70-3	4.00	2.04	0.00	0.44	2.19	6.91	7.15
25	Fluoranthene	206-44-0	2.38	1.55	0.00	0.24	1.58	5.00	5.18
26	Fluorene	86-73-7	1.59	1.06	0.00	0.25	1.36	4.32	4.53
27	Phenanthrene	85-01-8	2.06	1.29	0.00	0.29	1.45	4.54	4.59
28	Pyrene	129-00-0	2.81	1.71	0.00	0.28	1.58	5.00	5.12
Validation dataset for soil porewater									
1	Triclosan	3380-34-5	1.73	1.55	0.47	0.45	1.81	5.34	3.89
2	Cyfluthrin	68359-37-5	1.51	2.52	0.05	1.13	3.01	6.42	4.75
3	9-Fluorenone	486-25-9	1.75	1.51	0.00	0.36	1.37	3.49	3.84
4	Benzo[a]pyrene	50-32-8	3.63	1.96	0.00	0.37	1.95	6.19	6.49
5	Benzo[g,h,i]perylene	191-24-2	4.07	1.90	0.00	0.45	2.08	6.65	7.03
6	Indeno(cd)pyrene	193-39-5	3.61	1.93	0.00	0.42	2.08	6.65	7.02
7	Octocrylene	6197-30-4	1.59	2.03	0.05	0.80	3.06	6.89	5.52

[1] UFZ-LSER Database (2018). [2] ChEMBL database (2018), using predicted values by ACD software.

Table S4.3. Dataset for LSER model for surface water DOC source. LSER descriptors, Log K_{OW}, Log K_{DOC}.

Record number	Chemical	CAS	E[1]	S[1]	A[1]	B[1]	V[1]	Log K_{OW}[2]	Log K_{DOC}
Training dataset for surface water									
1	Diflufenican	83164-33-4	2.40	1.06	0.26	1.30	2.44	4.94	5.10
2	4-Bromoaniline	106-40-1	1.19	1.19	0.31	0.30	0.99	2.28	4.00
3	Alachlor	15972-60-8	1.16	1.20	0.00	1.15	2.14	3.05	4.01
4	Diazinon	333-41-5	1.04	1.01	0.00	1.19	2.31	3.44	4.97
5	2,4-Dibromoaniline	615-57-6	1.37	1.19	0.27	0.29	1.17	3.52	3.96
6	Tributyl phosphate	126-73-8	-0.09	0.62	0.00	1.29	2.24	3.83	5.34
7	Triphenyl phosphate	126-73-8	1.75	1.78	0.00	1.05	2.37	4.59	4.98
8	Biphenyl	92-52-4	1.36	0.99	0.00	0.26	1.32	4.09	3.74
9	Chlorothalonil	1897-45-6	1.56	2.30	0.00	0.28	1.52	3.04	4.73
10	Chlorpyrifos	2921-88-2	1.59	0.92	0.00	1.01	2.15	5.00	5.03
11	Chlorpyrifos-methyl	5598-13-0	1.37	1.50	0.00	0.50	1.87	3.99	4.59
12	Dibutyl phthalate	84-74-2	0.70	1.27	0.00	0.95	2.27	4.75	4.99
13	Ethoprophos	13194-48-4	0.67	0.53	0.00	0.84	1.88	3.39	4.63
14	Hexachlorobutadiene	87-68-3	1.02	0.42	0.00	0.16	1.32	4.91	3.94
15	Metolachlor	51218-45-2	1.11	1.53	0.00	1.25	2.28	3.03	4.70
16	Naphthalene	91-20-3	1.34	0.92	0.00	0.20	1.09	3.36	4.21
17	Pendimethalin	40487-42-1	1.39	1.39	0.16	0.71	2.15	5.20	4.79
18	Pentachlorobenzene	608-93-5	1.33	0.92	0.06	0.00	1.33	5.22	4.68
19	Picoxystrobin	117428-22-5	1.28	1.94	0.00	1.27	2.47	3.47	4.92
20	Trans-chlorfenvinfos	470-90-6	1.21	1.56	0.00	0.99	2.33	4.52	4.82
21	Trifluralin	1582-09-8	0.99	1.72	0.00	0.60	2.20	4.56	4.75
22	Triclosan	3380-34-5	1.73	1.55	0.47	0.45	1.81	5.34	3.84
23	Triclabendazole	68786-66-3	3.07	1.68	0.37	1.07	2.24	5.44	4.96
24	Bromophos methyl a	2104-96-3	1.51	1.51	0.00	0.46	1.96	5.17	4.03
25	cis-Permethrin	54774-45-7	1.95	1.87	0.00	0.98	2.82	7.64	5.73
26	Cypermethrin	52315-07-8	2.05	1.94	0.00	1.15	2.97	6.41	5.15
27	trans-Permethrin	61949-77-7	1.95	1.88	0.00	0.98	2.82	7.64	5.61
28	Octocrylene	6197-30-4	1.59	2.03	0.05	0.80	3.06	6.89	5.19
Validation dataset for surface water									
1	Pirimiphos methyl	29232-93-7	1.78	1.52	0.31	2.05	2.09	6.62	4.94
2	2,4'-DDD	72-54-8	1.80	1.73	0.10	0.26	2.10	5.82	4.72
3	Anthracene	120-12-7	2.29	1.34	0.00	0.28	1.45	4.54	4.65
4	Hexachlorobenzene	118-74-1	1.49	0.75	0.00	0.09	1.45	5.75	5.08
5	Phenanthrene	85-01-8	2.06	1.29	0.00	0.29	1.45	4.54	4.32
6	Deltamethrin	52918-63-5	1.98	2.80	0.05	1.11	3.08	6.42	5.19

[1] UFZ-LSER database (Ulrich *et al.*, 2017). [2] ChEMBL database (2018), using predicted values by ACD software.

Table S4.4. Dataset for LSER model for wastewater DOC source. LSER descriptors, Log K_{OW}, Log K_{DOC}.

Record number	Chemical	CAS	E[1]	S[1]	A[1]	B[1]	V[1]	Log K_{OW}[2]	Log K_{DOC}
Training dataset for wastewater									
1	Nonylphenol	104-40-5	0.77	0.88	0.55	0.36	2.04	6.14	3.25
2	Carbamazepine	298-46-4	2.15	1.90	0.50	1.15	1.81	1.90	3.14
3	Terbutryn	886-50-0	1.43	1.23	0.12	0.99	1.94	3.38	2.80
4	Irgarol	28159-98-0	1.69	1.39	0.26	1.08	1.97	3.26	3.12
5	Benzo[a]pyrene	50-32-8	3.63	1.96	0.00	0.37	1.95	6.19	3.75
6	Chlorpyrifos	2921-88-2	1.59	0.92	0.00	1.01	2.15	5.00	3.12
7	Dibenzo[ah]anthracene	53-70-3	4.00	2.04	0.00	0.44	2.19	6.91	4.05
8	Methoxychlor	72-43-5	1.59	2.09	0.00	0.73	2.37	5.07	3.06
9	Metolachlor	51218-45-2	1.11	1.53	0.00	1.25	2.28	3.03	2.86
10	Pyrene	129-00-0	2.81	1.71	0.00	0.28	1.58	5.00	3.16

[1] UFZ-LSER database (Ulrich *et al.*, 2017). [2] ChEMBL database (2018), using predicted values by ACD software.

Table S4.5. Dataset for LSER model for Aldrich HA DOC source. LSER descriptors, Log K_{OW}, Log K_{DOC}.

Record number	Chemical	CAS	E^1	S^1	A^1	B^1	V^1	$LogK_{OW}^2$	Log K_{DOC}
Training dataset for Aldrich HA									
1	4-Chlorophenol	106-48-9	0.92	1.08	0.67	0.20	0.90	2.42	2.31
2	3-Chlorophenol	108-43-0	0.91	1.06	0.69	0.15	0.90	2.35	2.46
3	4-Bromophenol	106-41-2	1.08	1.17	0.67	0.19	0.95	2.58	2.34
4	2,4,6-Trimethylphenol	527-60-6	0.86	0.81	0.30	0.45	1.20	2.94	2.29
5	4-Chloro-3-methylphenol	59-50-7	0.92	0.99	0.67	0.22	1.04	2.89	2.47
6	4-Chloro-3,5-dimethylphenol	88-04-0	0.98	0.94	0.61	0.26	1.18	3.38	2.83
7	4-Fluorophenol	371-41-5	0.67	0.97	0.63	0.23	0.79	1.84	2.32
8	4-Iodophenol	540-38-5	1.38	1.22	0.68	0.20	1.03	2.99	2.69
9	PCB 14	34883-41-5	1.65	1.18	0.00	0.16	1.57	5.28	4.63
10	PCB 18	37680-65-2	1.75	1.35	0.00	0.17	1.69	5.24	4.54
11	PCB 28	7012-37-5	1.76	1.33	0.00	0.15	1.69	5.67^3	4.95
12	PCB 35	37680-69-6	1.80	1.31	0.00	0.13	1.69	5.82^3	5.20
13	PCB 52	35693-99-3	1.90	1.48	0.00	0.15	1.81	5.83	5.12
14	PCB 77	32598-13-3	1.94	1.44	0.00	0.11	1.81	6.50	5.77
15	PCB 101	37680-73-2	2.04	1.61	0.00	0.13	1.94	6.44	5.60
16	PCB 118	31508-00-6	2.06	1.59	0.00	0.11	1.94	6.77	5.85
17	PCB 126	57465-28-8	2.11	1.57	0.00	0.09	1.94	7.03	6.39
18	PCB 180	35065-29-3	2.29	1.87	0.00	0.09	2.18	7.51	6.39
19	PCB 203	52663-76-0	2.48	2.00	0.00	0.06	2.30	7.65^3	5.96
20	PBDE 153	446255-03-4	3.09	1.58	0.00	0.21	2.43	7.40^3	6.71
21	PBDE 183	207122-16-5	3.51	1.65	0.00	0.57	2.61	8.19	6.63
Validation dataset for Aldrich HA									
1	4-Methylphenol	106-44-5	0.82	0.87	0.57	0.31	0.92	2.07	2.11
2	3,4-Dichlorophenol	95-77-2	1.02	1.24	0.93	0.00	1.02	3.16	2.87
3	2,4-Dimethylphenol	105-67-9	0.84	0.79	0.52	0.40	1.06	3.10	2.24
4	3-Methoxyphenol	150-19-6	0.88	1.17	0.59	0.39	0.97	1.82	2.00
5	PCB 72	41464-42-0	1.93	1.46	0.00	0.13	1.81	6.26^3	5.37
6	PCB 153	35065-27-1	2.18	1.74	0.00	0.11	2.06	6.92^3	6.10
7	PBDE 99	60348-60-9	2.71	1.59	0.00	0.07	2.26	7.31	6.35

[1] UFZ-LSER database (Ulrich *et al.*, 2017). [2] ChEMBL database (2018), using predicted values by ACD software. [3] PubChem Database (2018).

Table S4.6. LSER parameter ranges in different DOC datasets.

Dataset	Parameter range				
	E	S	A	B	V
All DOC	-0.09 - 4.07	0.42 - 2.8	0 - 1.01	0 - 2.05	0.79 - 3.08
Soil porewater	1.05 - 4	1.05 - 2.8	0 - 0.86	0.18 - 1.17	1.22 - 3.08
Surface water	-0.09 - 3.07	0.42 - 2.3	0 - 0.47	0 - 1.3	0.99 - 3.06
Wastewater	0.77 - 4	0.88 - 2.09	0 - 0.55	0.28 - 1.25	1.58 - 2.37
Aldrich HA	0.67 - 3.51	0.81 - 2	0 - 0.69	0.06 - 0.57	0.79 - 2.61

S5. Cross correlation matrices among LSER descriptors for different DOC datasets

Table S5.1. Cross correlation matrix among LSER descriptors in all DOC dataset.

All DOC		E	S	A	B
S	Pearson correlation	0.573			
	p	0			
A	Pearson correlation	-0.366	-0.27		
	p	0.001	0.021		
B	Pearson correlation	-0.107	0.256	-0.057	
	p	0.369	0.029	0.633	
V	Pearson correlation	0.322	0.649	-0.462	0.597
	p	0.006	0	0	0

Table S5.2. Cross correlation matrix among LSER descriptors in soil porewater dataset.

Soil porewater		E	S	A	B
S	Pearson correlation	0.264			
	p	0.175			
A	Pearson correlation	-0.081	0.244		
	p	0.683	0.21		
B	Pearson correlation	-0.229	0.563	0.458	
	p	0.24	0.002	0.014	
V	Pearson correlation	-0.015	0.666	0.15	0.842
	p	0.941	0	0.445	0

Table S5.3. Cross correlation matrix among LSER descriptors in surface water dataset.

Surface water					
		E	S	A	B
S	Pearson correlation	0.491			
	p	0.008			
A	Pearson correlation	0.444	0.011		
	p	0.018	0.955		
B	Pearson correlation	0.085	0.19	-0.153	
	p	0.668	0.333	0.437	
V	Pearson correlation	0.26	0.51	-0.239	0.798
	p	0.181	0.006	0.221	0

Table S5.4. Cross correlation matrix among LSER descriptors in wastewater dataset.

Wastewater					
		E	S	A	B
S	Pearson correlation	0.675			
	p	0.032			
A	Pearson correlation	-0.408	-0.333		
	p	0.242	0.346		
B	Pearson correlation	-0.521	-0.197	0.105	
	p	0.123	0.585	0.773	
V	Pearson correlation	-0.249	0.034	-0.28	0.267
	p	0.487	0.927	0.434	0.456

Table S5.5. Cross correlation matrix among LSER descriptors in Aldrich HA dataset.

Aldrich HA					
		E	S	A	B
S	Pearson correlation	0.842			
	p	0			
A	Pearson correlation	-0.771	-0.725		
	p	0	0		
B	Pearson correlation	0.065	-0.353	0.19	
	p	0.779	0.116	0.41	
V	Pearson correlation	0.964	0.869	-0.876	-0.025
	p	0	0	0	0.915

S6. Approach used for organic acids and bases and training and validation datasets

Text S6.1. Approach used to develop regressions for organic acids and bases.

The overall K_{OW} (or P) of an ionizable chemical for at given pH is:

$$K_{OW} = \varphi_{neutral}\, P_{neutral} + \varphi_{ion}\, P_{ion} \tag{1}$$

Where $\varphi_{neutral}$ and φ_{ion} are respectively the fractions of chemical in neutral and ionic state.

Similarly, since the overall K_{OC} derives from the contribution of both, the K_{OC} of the neutral ($K_{OC\ neutral}$) and ionic ($K_{OC\ ion}$) fractions, it can be written as:

$$K_{OC} = \varphi_{neutral}\, K_{OC\ neutral} + \varphi_{ion}\, K_{OC\ ion} \tag{2}$$

Considering that K_{OC} of the neutral fraction can be predicted by linear regression as:

$$Log\ K_{OC\ neutral} = a\ Log\ P_{neutral} + b \tag{3}$$

and for the ionic fraction as:

$$Log\ K_{OC\ ion} = c\ Log\ P_{ion} + d \tag{4}$$

Since Log $P_{neutral}$ and Log P_{ion} are related (e.g. Log P_{ion} = Log $P_{neutral}$ – 3.5) (Trapp and Horobin, 2005), Log P_{ion} in equation 2 can be substituted to give:

$$Log\ K_{OC} = Log\ (\varphi_{neutral}\ 10^{a\ Log\ P_{neutral} + b} + \varphi_{ion}\ 10^{c\ Log\ P_{neutral} + d}) \tag{5}$$

Chemical dissociation at a specific pH can be calculated according to the Henderson-Hasselbalch equation:

$$\varphi_{neutral} = \frac{1}{1+\ 10^{a(pH-pKa)}} \tag{6}$$

$$\varphi_{ion} = 1 - \ \varphi_{neutral} \tag{7}$$

Where a is equal to 1 for acids and to -1 for bases.

Franco and Trapp (2008) separately derived regressions for weak (pKa > 7.5) and strong acids (pKa < 4) and for weak (pKa < 3) and strong bases (pKa > 7.5) representing neutral and ionic chemicals respectively and then combined the regressions obtained (as shown in equation 6).

The regression for weak acids ($R^2 = 0.81$) was:

$$Log\ K_{OC}\ =\ 0.54\ Log\ P_{neutral} +\ 1.11 \tag{8}$$

The regression for strong acids ($R^2 = 0.04$) was:

$$Log\ K_{OC}\ =\ 0.11\ Log\ P_{neutral} +\ 1.54 \tag{9}$$

The final equation for acids ($R^2 = 0.54$) was:

$$Log\ K_{OC} =\ Log\ (\varphi_{neutral}\ 10^{0.54\ Log\ P_{neutral}+\ 1.11} +\ \varphi_{ion}\ 10^{0.11\ Log\ P_{neutral}+\ 1.54} \tag{10}$$

The regression for weak bases ($R^2 = 0.83$) instead was:

$$Log\ K_{OC} = 0.42\ Log\ P_{neutral} + 1.34 \tag{11}$$

The regression for strong bases ($R^2 = 0.75$) was:

$$Log\ K_{OC} = 0.47\ Log\ P_{neutral} + 1.95 \tag{12}$$

The combined equation was for bases ($R^2 = 0.60$) was:

$$Log\ K_{OC} = Log\ (\varphi_{neutral}\ 10^{0.42\ Log\ P_{neutral} + 1.34} + \varphi_{ion}\ 10^{0.47\ Log\ P_{neutral} + 1.95} \tag{13}$$

Then they corrected the equation for bases with a factor accounting for the diffusion-limited transport of the cations through the soil organic matter and applied the final equations to the training dataset to estimate the pH giving the best fit with data ($pH_{optimal}$ = 5.8 for acids and 4.5 for bases). Later (Franco *et al.*, 2009), they corrected the equations proposed with a semi-empirical factor to calculate soil pH dependent K_{OC}.

In the present study, a similar approach was used for D_{DOC} estimation, calculating the percentage of dissociation for each chemical in the dataset.

Table S6.1. Dataset for organic acids. LSER descriptors, Log K_{OW}, acid (A-Pka) dissociation constant of the target chemicals, Log D_{DOC}, pH of the experiment and calculated neutral and ionic fractions.

Record number	Chemical	CAS	E[1]	S[1]	A[1]	B[1]	V[1]	$LogK_{OW}$[2]	A-Pka[2]	Log D_{DOC}	pH	$\varphi_{neutral}$	φ_{ion}
	Training dataset for neutral organic acids												
1	4-Methylphenol	106-44-5	0.82	0.87	0.57	0.31	0.92	2.07	10.21	2.11	7.3	>0.99	<0.01
2	4-Chlorophenol	106-48-9	0.92	1.08	0.67	0.20	0.90	2.42	9.47	2.31	7.3	0.99	0.01
3	3-Chlorophenol	108-43-0	0.91	1.06	0.69	0.15	0.90	2.35	9	2.46	7.3	0.98	0.02
4	4-Bromophenol	106-41-2	1.08	1.17	0.67	0.19	0.95	2.58	9.34	2.34	7.3	0.99	0.01
5	4-Chloro-3-methylphenol	59-50-7	0.92	0.99	0.67	0.22	1.04	2.89	9.63	2.47	7.3	>0.99	<0.01
6	4-Chloro-3,5-dimethylphenol	88-04-0	0.98	0.94	0.61	0.26	1.18	3.38	9.76	2.83	7.3	>0.99	<0.01
7	3,4-Dichlorophenol	95-77-2	1.02	1.24	0.93	0.00	1.02	3.16	8.56	2.87	7.3	0.95	0.05
8	Oxybenzone	131-57-7	1.65	1.63	0.00	0.62	1.74	4	7.56	3.33	5.38	0.99	0.01
9	Estradiol	50-28-2	1.80	1.77	0.86	1.10	2.20	4.15	10.27	3.23	5.38	>0.99	<0.01
10	Triclosan	3380-34-5	1.73	1.55	0.47	0.45	1.81	5.34	7.8	3.89	5.38	>0.99	<0.01
11	3-Methoxyphenol	150-19-6	0.88	1.17	0.59	0.39	0.97	1.82	9.59	2.00	8.3	0.95	0.05
12	4-Fluorophenol	371-41-5	0.67	0.97	0.63	0.23	0.79	1.84	9.92	2.32	7.3	>0.99	<0.01
13	4-Iodophenol	540-38-5	1.38	1.22	0.68	0.20	1.03	2.99	9.3	2.69	7.3	0.99	0.01
	Training dataset for dissociated organic acids												
1	2,6-Dichlorophenol	87-65-0	0.90	0.86	0.36	0.24	1.02	2.9	7.02	2.58	7.3	0.34	0.66
2	2,4,6-Trichlorophenol	88-06-2	1.01	0.80	0.60	0.15	1.14	3.77	6.59	2.69	7.3	0.16	0.84
3	2,3,6-Trichlorophenol	933-75-5	1.01	0.88	0.62	0.15	1.14	3.64	6.06	2.72	7.3	0.05	0.95
4	2,3,4,6-Tetrachlorophenol	58-90-2	1.10	0.87	0.50	0.15	1.26	4.44	5.63	2.91	7.3	0.02	0.98
5	Pentachlorophenol	87-86-5	1.22	0.91	0.66	0.06	1.39	5.12	4.68	3.00	7.3	<0.01	>0.99
	Validation dataset												
1	3,5-Dichlorophenol	591-35-5	1.02	1.02	0.92	0.00	1.02	3.16	8.04	2.84	7.3	0.85	0.15
2	2,4-Dichlorophenol	120-83-2	0.96	0.82	0.54	0.17	1.02	3.1	8.05	2.50	7.3	0.85	0.15
3	2,4,6-Trimethylphenol	527-60-6	0.86	0.81	0.30	0.45	1.20	2.94	10.97	2.29	7.3	>0.99	<0.01
4	2,5-Dichlorophenol	583-78-8	0.96	0.84	0.52	0.18	1.02	3.02	7.53	2.58	7.3	0.63	0.37
5	2,4-Dimethylphenol	105-67-9	0.84	0.79	0.52	0.40	1.06	2.5	10.61	2.24	7.3	>0.99	<0.01

[1] UFZ-LSER database (Ulrich *et al.*, 2017). [2] ChEMBL database (2018), using predicted values by ACD software.

Table S6.2. Dataset for organic bases. LSER descriptors, Log Kow, base (B-Pka) dissociation constant of the target chemicals, Log D_{DOC}, pH of the experiment and calculated neutral and ionic fractions.

Record number	Chemical	CAS	E^1	S^1	A^1	B^1	V^1	$LogK_{OW}^2$	B-Pka^2	Log D_{DOC}	pH	$\varphi_{neutral}$	φ_{ion}
	Training dataset for neutral organic bases												
1	4-Bromoaniline	106-40-1	1.19	1.19	0.31	0.30	0.99	2.28	3.9	4.00	7.8	>0.99	<0.01
2	Alachlor	15972-60-8	1.16	1.20	0.00	1.15	2.14	3.05	1.2	4.01	7.8	>0.99	<0.01
3	Pirimiphos methyl	29232-93-7	1.78	1.52	0.31	2.05	2.09	6.62	3.74	4.94	7.8	>0.99	<0.01
4	Diazinon	333-41-5	1.04	1.01	0.00	1.19	2.31	3.44	1.21	4.97	7.8	>0.99	<0.01
5	2,4-Dibromoaniline	615-57-6	1.37	1.19	0.27	0.29	1.17	3.52	1.83	3.96	7.8	>0.99	<0.01
6	Terbutryn	886-50-0	1.43	1.23	0.12	0.99	1.94	3.38	4.03	2.80	7.8	>0.99	<0.01
7	Irgarol	28159-98-0	1.69	1.39	0.26	1.08	1.97	3.26	4.13	3.12	7.8	>0.99	<0.01
8	Acridine	260-94-6	2.36	1.32	0.00	0.58	1.41	3.45	5.56	4.29	7.8	0.99	0.01
9	4-Bromoaniline	106-40-1	1.19	1.19	0.31	0.30	0.99	2.28	3.9	4.00	7.8	>0.99	<0.01
	Training dataset for dissociated organic bases												
1	Chlorpromazine	50-53-3	2.16	1.57	0.00	1.01	2.41	5.18	9.41	4.33	5.16	<0.01	>0.99
2	Triflupromazine	146-54-3	1.66	1.37	0.00	1.00	2.48	5.16	9.4	4.26	5.16	<0.01	>0.99
3	Clotrimazol	23593-75-1	2.55	2.60	0.00	1.21	2.62	4.92	6.12	4.63	6.32	0.61	0.39
4	Promazine	58-40-2	2.05	1.49	0.00	1.08	2.28	4.69	9.43	3.76	6.93	<0.01	>0.99

S7. DOC descriptors calculated by LSER for different DOC datasets

Table S7.1. DOC descriptors calculated by LSER for different DOC datasets: all DOC, soil porewater, surface water, wastewater, Aldrich HA (regressions with all LSER parameters).

All DOC				
Parameter		**SE**	**T**	***p***
c	2.34	0.35	6.63	0.00
e	0.68	0.12	5.50	0.00
s	-0.55	0.25	-2.16	0.04
a	-1.34	0.36	-3.73	0.00
b	-0.68	0.26	-2.62	0.01
v	1.29	0.25	5.06	0.00

Soil porewater				
Parameter		**SE**	**T**	***p***
c	1.76	0.34	5.23	0.00
e	0.88	0.11	7.73	0.00
s	-0.26	0.24	-1.09	0.29
a	-0.89	0.48	-1.86	0.08
b	-1.83	0.52	-3.56	0.00
v	1.41	0.29	4.93	0.00

Surface water				
Parameter		**SE**	**T**	***p***
c	3.26	0.31	10.65	0.00
e	0.07	0.16	0.44	0.67
s	-0.04	0.20	-0.21	0.84
a	-0.59	0.65	-0.91	0.37
b	0.10	0.32	0.30	0.77
v	0.66	0.27	2.41	0.03

Wastewater				
Parameter		**SE**	**T**	***p***
c	1.06	0.24	4.43	0.01
e	0.44	0.03	12.84	0.00
s	-0.26	0.06	-3.98	0.02
a	0.73	0.11	6.54	0.00
b	-0.24	0.07	-3.71	0.02
v	0.86	0.10	8.40	0.00

Aldrich HA				
Parameter		**SE**	**T**	***p***
c	2.17	0.77	2.82	0.01
e	0.88	0.43	2.04	0.06
s	-0.52	0.73	-0.71	0.49
a	-1.18	0.64	-1.84	0.09
b	-3.18	1.03	-3.09	0.01
v	1.47	0.88	1.66	0.12

SE: standard error. T: t value.

S8. Predicted *vs.* observed Log KDOC in the validation dataset

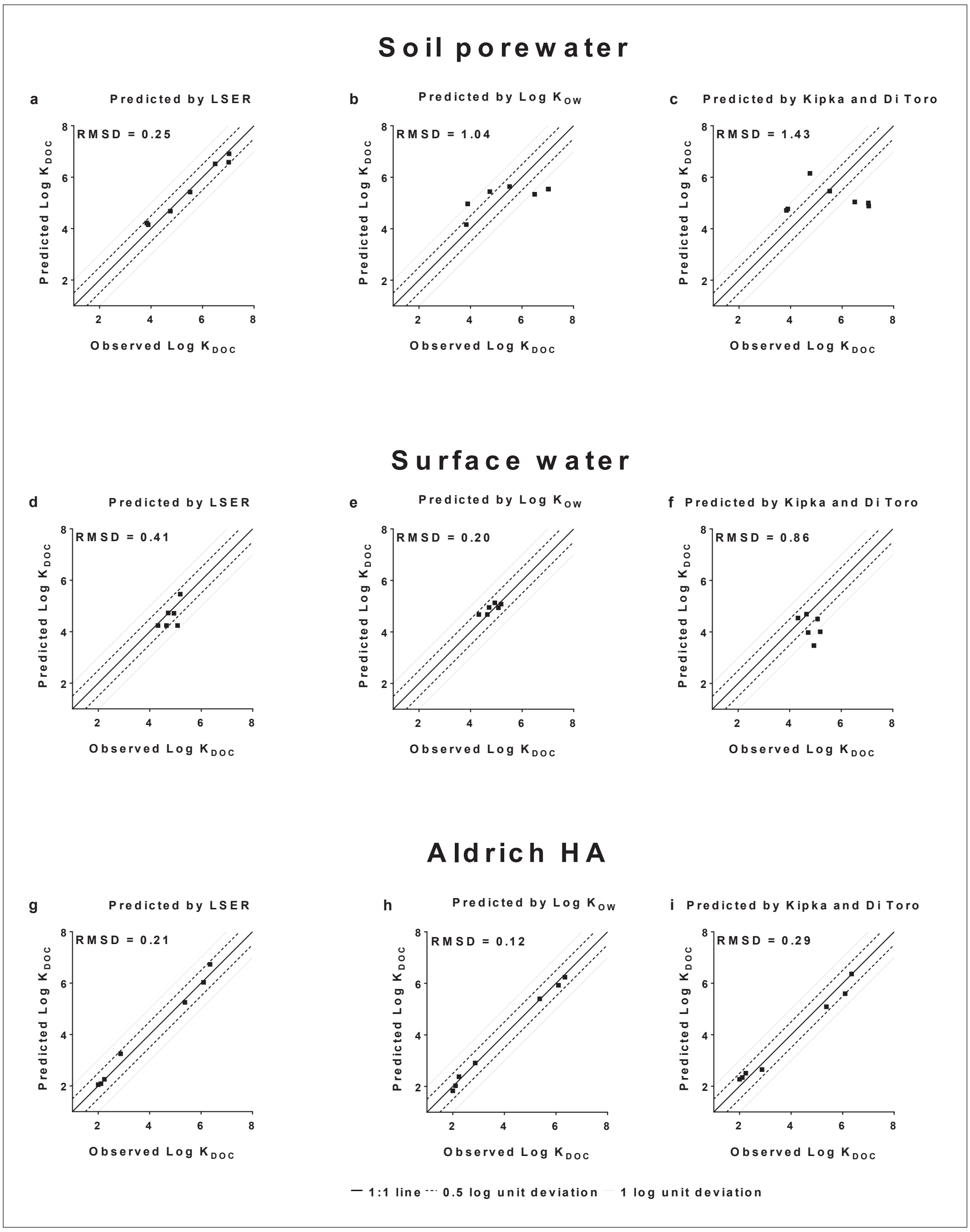

Figure S8.1. Predicted *vs.* observed Log K_{DOC} in the validation dataset for: soil porewater by LSER model (a), soil porewater by Log K_{OW} (b), soil porewater by Kipka and Di Toro LSER model (c); surface water by LSER model (d), surface water by Log K_{OW} (e), surface water by Kipka and Di Toro LSER model (f); Aldrich HA by LSER model (g), Aldrich HA by Log K_{OW} (h), Aldrich HA by Kipka and Di Toro LSER model (i).

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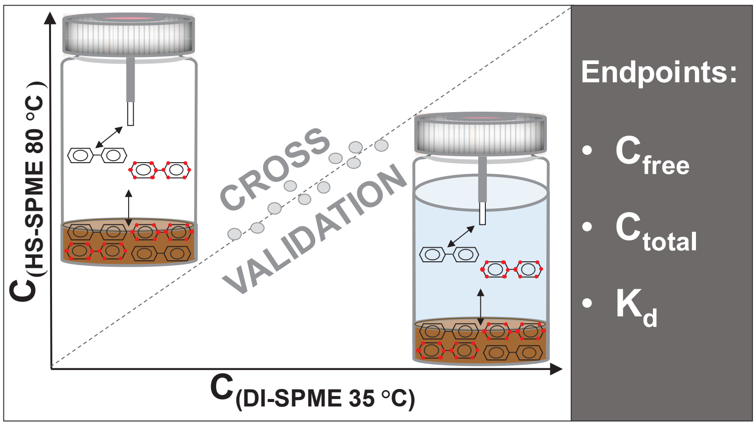
Paper V: Accelerated equilibrium sampling of hydrophobic organic chemicals in solid matrices – automated SPME with reduced equilibration times



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Abstract

Equilibrium sampling of hydrophobic organic chemicals (HOCs) is increasingly used to measure freely dissolved concentrations and chemical activities in sediments and soils. However, for the most hydrophobic chemicals (Log $K_{ow} > 6$) such equilibrium sampling requires very long sampling times in the order of weeks to months. The aim of the present study was to explore two strategies for markedly increasing the HOC mass transfer from matrix to sampler with the overall goal to shorten equilibration times down to a few hours. Two Solid Phase Microextraction (SPME) approaches were thus developed and tested in sediment and soil contaminated by polychlorinated biphenyls (PCBs). In the first method, the SPME fiber was immersed directly in the aqueous suspension of the sample under vigorous agitation. In the second method equilibration took place via the headspace and was accelerated by elevating the temperature. Both methods were calibrated by passive dosing from preloaded silicone rods and yielded similar results thereby cross-validating each other. Headspace-SPME at 80 °C provided fast equilibration within approximately two hours without contacting the sample and thus avoiding fiber fouling. Finally, by using ^{13}C labelled PCB standards, total concentrations were simultaneously measured, which in turn allowed calculation of matrix–water distribution coefficients.

Introduction

Risk assessment of hydrophobic organic chemicals (HOCs) in contaminated sediment and soil is in many regulatory programs still based on measurements of total concentrations (C_{total}) that include both freely dissolved and matrix associated HOC molecules.[1] It is increasingly recognized that C_{total} is poorly connected to the actual HOC exposure and risk, and that C_{free} is better linked to bioavailability, potential for bioaccumulation, toxicity and remediation processes.[1–4] Freely dissolved concentrations are the effective concentrations for many spontaneous processes including diffusion and partitioning, which also can be utilized in passive sampling methods, where a reference phase is introduced as sampler into the sample to measure $C_{free.}$[5–9] A suite of *ex situ*[7–11] and *in situ*[12,13] passive sampling methods have thus been developed and applied during the last 20 years, and recent cross validation and inter-laboratory studies have shown good performance and agreement between these methods.[13,17,18]

Very long equilibration times of weeks or even months[19] remain the biggest challenge for the various ways to perform equilibrium sampling of HOCs in solid matrices as soil and sediment.[4,6] *In situ* sampling generally requires that a sampling device is positioned in the environment on a first field sampling campaign and then retrieved several weeks later on a second campaign. Equilibrium is often not reached and requires then dedicated disequilibrium corrections using kinetic models and performance reference compounds.[13,17,18] *Ex situ* sampling in the laboratory can be combined with various ways of agitation in order to speed up the mass transfer and thus sampling kinetics.[20] Often equilibration still requires several weeks for the most hydrophobic pollutants such as polychlorinated biphenyls (PCBs).[5,15,21,22] Reducing equilibration times to hours or minutes would make such method more practical and time efficient. Markedly reduced equilibration times in the minute range could even allow operating equilibrium sampling on an autosampler directly on a gas chromatograph mass spectrometer (GC-MS).

The primary goal of the present study is to find a sound and efficient approach to significantly accelerate the HOC mass transfer from the sample matrix to the sampler with the eventual goal to allow fully automated equilibrium solid phase microextraction (SPME) and GC-MS analysis of even highly hydrophobic organic chemicals, such as PCBs. The rate limiting steps for the mass transfer to the sampler can be slow desorption kinetics from the sample matrix[23,24] and molecular diffusion through the unstirred boundary layer (UBL) surrounding the sampler fiber.[25–30] Faster kinetics can then be reached by agitation,[20] optimizing the sample/fiber volume ratios,[31] adding contaminant carrier to enhance mass transfer through the UBL[26,32] or by using thinner SPME coating.[15,32,33] Placing the sampler in the headspace above the sample at elevated temperature is another approach that could speed up sampling kinetics, since elevated temperatures will increase headspace concentrations and thus the concentration gradient driving the HOC partitioning into the sampler. Additionally, elevated temperatures will increase the energetic state of the molecules and thus their diffusion coefficients. Elevated temperatures will reduce the PCB partition coefficients between matrix and headspace and correspondingly increase the partition coefficients between headspace and SPME coating[20], whereas we only expect a very minor temperature effect on the resulting partition coefficient between sample and sampler coating. Headspace equilibrium sampling at elevated temperature would be a sound way to determine freely dissolved concentrations and chemical activity at lower temperatures, if the matrix to coating partition coefficients are largely temperature independent.

In this study, two automated equilibrium SPME methods were developed and then applied to PCB contaminated soil and sediment: 1) direct immersion (DI)-SPME at 35 °C and vigorous shaking was mainly set up as a reference method and 2) headspace (HS)-SPME at 80 °C was introduced as a new equilibrium sampling method with shortened equilibration times and without physical contact between sample and sampler to avoid fouling. The sampling kinetics of these two methods were compared, and the obtained results were then used for cross-validation and for supporting the working hypothesis that PCB partitioning between organic carbon and polydimethylsiloxane (PDMS) coating is largely temperature independent. Additionally, total PCB concentrations were measured based on spiked ^{13}C labelled PCB standards,[34] and sample specific K_d values were finally determined as the ratio of C_{total} over C_{free}.

To avoid potential artefacts of spiking poorly soluble chemicals in aqueous solutions a novel external calibration approach with passive dosing vials was developed and applied to determine the silicone concentration at equilibrium ($C_{silicone}$), which was then converted to C_{free} using the silicone-water partitioning coefficient ($K_{silicone\text{-}water}$).

Working principle.

The working principle of the proposed approaches is summarized in Table 1.

Table 1. Working principles of the equilibrium DI and HS-SPME methods in comparison.

	DI- SPME	**HS-SPME**
Equilibrium sampling	Equilibrium sampling with the fiber within the sample matrix, while speeding up mass transfer by vigorous agitation.	Equilibrium sampling with the fiber within headspace above the sample, while speeding up mass transfer by an elevated temperature (80 °C).
Calibration 1	Determination of $C_{silicone}$ using passive dosing from a PCB loaded silicone for external calibration.	
Calibration 2	Determination of C_{total} based on ^{13}C labelled PCBs: $C_{total} = \frac{mass_{13C-PCB}}{mass_{solid}} \cdot \frac{Peak\ area_{13C-PCB}}{Peak\ area_{12C-PCB}}$ (**1**) Labelled standard are assumed to have identical partitioning to native chemicals in a multi-phase environment[34] and C_{total} of native PCBs are therefore calculated from the known total concentrations of the added 13-C PCBs.	

Cross validation	$$C_{free} = \frac{C_{silicone}}{K_{silicone-water}} \; \mathbf{(2)}$$	If the working hypothesis is valid: $C_{silicone\ (from\ DI\text{-}SPME)} = C_{silicone\ (from\ HS\text{-}SPME)}$ Then: $$C_{free} = \frac{C_{silicone\ (from\ HS-SPME)}}{K_{silicone-water}}$$
K_d and K_{oc} calculation	$K_d = \frac{C_{solid}}{C_{free}} \approx \frac{C_{total}}{C_{free}}$ **(3)** where C_{solid} is the concentration in the solid matrix. $K_{oc} = \frac{K_d}{f_{oc}}$ **(4)** where K_{oc} is the soil-water distribution coefficient normalized to the fraction of organic carbon (f_{oc})	

Equilibrium HS-SPME can be used to determine chemical activity and freely dissolved concentrations (C_{free}) in water phase of chemicals capable of volatilizing in the headspace.[35] Therefore, increasing temperatures in HS-SPME can be a faster alternative approach to the traditional DI-SPME since it raises the concentration of chemical in headspace to detectable levels. If we compare the DI-SPME $K_{silicone-water}$ partition coefficient:

$$K_{silicone-water} = C_{silicone}/C_{free} \; \mathbf{(5)}$$

to the HS-SPME Ksilicon-air partition coefficient:

$$K_{silicone-air} = C_{silicone}/C_{air} \; \mathbf{(6)}$$

since SPME is a monitor of chemical activity,[35] the following relationship exists, at equilibrium, at a certain specified temperature (e.g. 35 °C):

$$K_{silicone-water}\, C_{free} = K_{silicone-air}\, C_{air} \; \mathbf{(7)}$$

Where C_{air} is the concentration of the target analyte in the headspace.

This equation can be also written as:

$$\frac{K_{silicone-water}}{K_{silicone-air}} = \frac{C_{air}}{C_{free}} = K_{AW} \textbf{ (8)}$$

K_{AW} is the air-water partition coefficient at equilibrium, which notably changes with temperature. K_{AW} is increasing when temperature increases, due to the different response of the air and water solubilities to temperature variation. This means that the decrease of $K_{silicone\text{-}air}$ with temperature increase will be compensated by the increase in C_{air} and allow for HS-SPME measurement since C_{air} would be detectable by the SPME fibers.

Materials and methods

Chemicals and materials. Polychlorinated biphenyls (IUPAC PCB congeners 28, 52, 101, 118, 138, 153, 180) (purity ≥ 99%, concentration: 100 ng μL^{-1} in methanol) and the corresponding ^{13}C labelled standards (purity > 99%; concentration: 1000 ng mL^{-1} in nonane) were purchased from Dr. Ehrenstorfer GmbH (Germany) and Cambridge Isotope Laboratories (MA, U.S.A) respectively. Methanol (purity ≥ 99.9%) and ethyl acetate (purity ≥ 99.7%) were purchased from Sigma-Aldrich and ethanol (purity > 99.8%) from VWR International (Radnor, Pennsylvania). Humic acid (HA) (sodium salt) was purchased from Sigma-Aldrich (Lot Number: BCBG7429V, Carbon content: 40.33%). Ultrapure water (PURELAB Flex 2, Holm & Halby technologies) was used for sample and calibrant preparation. Translucent polydimethylsiloxane (PDMS) silicone rods without whitening agent (diameter: 3 mm) were custom made by Altecweb (Victoria, United Kingdom, product code: 136-8380). Solid phase microextraction fiber devices with 7 μm (bonded) PDMS coating were purchased from Supelco (Bellefonte, Pennsylvania).

Sediment and soil samples. PCB contaminated sediment with concentrations of target congeners in the order of hundreds to thousands of µg kg^{-1} (d.w.) and total organic carbon (OC) content of 3.6% (Table S1.1) originated from New Bedford Harbor (Massachusetts, U.S.A.). [13,36] The sediment was obtained from the US Army Corps of Engineers Research and Development Center (Vicksburg, MI, USA) in 2014 and then stored at 4 °C until analysis. Contaminated soil[37,38] containing PCB concentrations in the order of hundreds of µg kg^{-1} (d.w.) (Table S1.2) was obtained in July 2016 from a rhizoremediation experiment from the National Priority Contaminated Site Brescia-Caffaro (Brescia, Northern Italy) and stored dry at 4 °C until analysis. This soil has a sandy loam texture and an OC content of 1.5± 0.2% (Table S1.2).[38]

Direct immersion and headspace SPME. For the DI-SPME, 4 g of sample were placed in 20 mL amber vials with PTFE lined caps (Mikrolab, Aarhus, Denmark), ultrapure water (12 mL) was added and allowed to equilibrate for at least 48 hours on a roller mixer before SPME sampling. A headspace (~ 4-5 mL) was left in the vial to facilitate the mixing. Caps were changed before SPME analysis and vial necks gently cleaned on the inside with lint free tissue. The liquid to solid ratio (L:S, L kg^{-1}) 3:1 was selected as the optimum after testing different options (L:S 1:1, 2:1, 3:1 for sediments and L:S 2:1, 3:1 for soil) (S4). For the HS-SPME the samples (4 g) were directly put into the vial prior GC-MS analysis without adding water. In the DI-SPME experiment with labelled standards to determine the C_{total}, just 0.5 g of soil were used to reduce the amount of ^{13}C standards needed and thereby lower cost of the analysis. The soil was spiked with 50 µL of ^{13}C PCBs (1 ng μL^{-1} in nonane) plus 13.5 mL of water. To allow solvent evaporation, samples were kept open in the fume hood for 2 hrs and then left closed 24 hours on a roller mixer before adding the water.

Humic acid solution preparation. A solution containing 300 mg L^{-1} of Aldrich HA (≈120 mg OC L^{-1}) was prepared and 12 mL of this solution added to some of the soil samples to speed-up sampling kinetics of DI-SPME. This concentration was selected to be high enough to potentially act effective as mass carriers of PCBs [39,40] while trying to avoid their depletion. The added amount of HA corresponds to 0.1% (0.04% if expressed as OC) of the mass of the sample against a natural OC content in soil samples of 1.5%. The solution was stirred with a magnetic stir bar at 450 rpm for 1 hour, sonicated for 1 hour to enhance the HA powder dissolution, adjusted to pH 7.5 with NaOH (0.1 M) to increase the HA solubility, stirred again overnight and finally sonicated for 1 h before use. Based on literature,[41,42] 7 days were selected to equilibrate the samples with the added HA before SPME sampling.

Silicone rod preparation and passive dosing calibration. An external calibration with the passive dosing vials was used to determine $C_{silicone}$, which then was converted to C_{free} using $K_{silicone-water}$ (see Table S2.1).[46] The passive dosing vials was generated by initially rinsing the silicone rods with tap water, immersed in ethyl acetate (overnight), immersed in ethanol (overnight) and finally dried at 180 °C for 2 hours. Each calibrant was then prepared with around 2 g of silicone rod in 20 mL amber autosampler vials. A methanol/water solution 1:1 (v/v) (14 mL) was used as medium to enhance the chemical mass transfer and allow faster equilibration.[43–45] The methanol was spiked with (non-labelled) PCBs and mixed on a roller mixer for 1 h at 30 rpm. After that, ultrapure water was slowly added to gradually push PCBs into the silicone rods and to avoid PCB precipitation: 2.00 mL of water were added and the vial was rolled on a mixer overnight; later on additional 2.00 mL of water were added and the vial was rolled again overnight and finally 3.00 mL of water were added and rolled for 15 days at 20 °C. The methanol in the solution was used to speed up the mass transfer from the silicone rod to the SPME coating while avoiding any significant PCB depletion of the rods. The absence of depletion was confirmed by three-phase mass balance calculations attesting that 98.5% (PCB 28) to 99.9% (PCB 180) of the PCB will remain in the silicone rod. SPME fibers were equilibrated in these passive dosing vials in order to transfer the loaded silicone donor concentration (silicone rod) to the silicone acceptor (SPME coating). The novel calibration approach proposed aims to: 1) avoid potential artefacts of spiking poorly soluble chemicals in aqueous solutions (e.g. losses to the glassware), 2) shorten sampling time for automatization and 3) be easy to setup and perform.

Chemical analysis. Automated SPME was performed with a PAL3 autosampler (CTC Analytics, Zwingen, Switzerland) mounted on a Gas Chromatography Mass Spectrometry (GC-MS) (Agilent Technologies 7890B/5977A GC/MSD). An Agilent 122-5562 DB-5ms Ultra Inert 60 m x 0.25 mm, 0.25 μm column was used for separating target PCBs (28, 52, 101, 118, 138, 153, 180) selected as model compounds. The SPME fiber was preconditioned at 320 °C for 1 hour prior use. Direct-SPME was performed at 35 °C by immersion of the fiber (penetration depth: 35 mm) into the sample shaken at 500 rpm for one hour. Thermal desorption was performed within the injector hold at a temperature of 315 °C in splitless mode with helium as carrier gas with a flow of 1.3 mL min^{-1}. Oven start temperature was 80 °C for 10 minutes, followed by a ramp of 25 °C min^{-1} to 180 °C held 2 minutes, by a second ramp of 2 °C min^{-1} to 238 °C held 2 minutes and by a final ramp of 25 °C min^{-1} to 300 °C held 3.3 minutes (total GC program length: 53 minutes). In HS-SPME the same GC-MS program was used varying just the penetration depth (20 mm) and sampling temperature (80 °C). PCBs were identified in SIM (Selected Ion Mode) using one ion for identification and one for quantification for each chlorination degree (Table S3.1). Method detection limits[47] (Table S3.2) ranged from 11 (PCB 138, 180) to 241 (PCB 52) pg L^{-1}. Samples were prepared in duplicates or triplicates. See S3 for further details in quality assurance and control (QA/QC) measurements and method detection limit determination.

Determining SPME sampling kinetics

Temporal series were performed to determine sampling kinetics in sediment (15, 30, 60, 90, 180 and 360 minutes for DI-SPME; 30, 60, and 120 minutes for HS-SPME) and soil (60, 120 and 240 minutes both for DI-SPME and HS-SPME). The PCB signals (calibrated to silicone concentrations) were fitted to a first-order one-compartment model (GraphPad Prism 7, GraphPad, CA, U.S.A.) as function of the sampling time (t) (hours):

$$C_{silicone\ (t)} = C_{silicone\ (eq.)} \cdot (1 - e^{-kt}) \mathbf{(9)}$$

where $C_{silicone(eq)}$ is the silicone concentration at equilibrium and k (h^{-1}) is the fiber sorption uptake rate constant. The time to reach 95% of equilibrium (t_{95}) was calculated as:

$$t_{95} = \frac{ln_{20}}{k} \mathbf{(10)}$$

Statistical analysis.

Data were illustrated as: 1) average ± standard deviation (SD), 2) average ± standard error of mean (SEM) or 3) average ± 95% confidence interval (CI). Relative standard deviation (RSD) was calculated as the ratio of the standard deviation to the mean and expressed as percentage. Statistical analysis (Student's t test, $\alpha = 0.05$; one-way analysis of variance, ANOVA, $\alpha = 0.05$) were performed with the software SIGMASTAT 3.0 (Systat Software, Inc, CA, U.S.A.).

RESULTS AND DISCUSSION

Passive dosing calibration. Passive dosing from a pre-loaded polymer turned out to be an effective and practical method for transferring analyte concentrations from a silicone donor to the silicone coating of the SPME fiber, which then allowed the external calibration for automated SPME operation. By using methanol/water solution, equilibrium was reached rapidly[43,44] as confirmed by extracting the same vial for 1 hour and 2 hours with less than 10 % difference in PCB concentration. The methanol reduced the impact of potential artefacts related to incomplete solubility of these compounds in water and to losses to the vessel (e.g. glass walls, lid).[48]. Finally, this new approach has the advantage of simplicity and suitability for automatization. Considering the volume ratio between SPME fiber and silicone rod (0.028 µL[20] vs. ~ 2 mL) calibrants can be extracted again and again for more than 3500 times before significant depletion (> 5%).

DI-SPME. In sediment samples (Figure 1a, Figure S5.1) equilibration time was reasonably fast (t_{95} within 3 hours for all congeners) with similar rate constants among different congeners (Table S5.1, Figure S7.1). Some constituents in sediment porewater such as dissolved organic carbon (DOC)/colloids can enhance the mass transfer toward the SPME fiber,[26] especially for more hydrophobic congeners with strong affinity for these phases[32,40,49] resulting in rate constants independent of chemical hydrophobicity.

In soil suspension samples, sampling kinetics were slower for PCB 118, 138, 153 and 180 still being in the kinetic phase after 4 hours (Figure 1c, Figure S5.2). The congener-specific rate constants were up to factor 14 smaller for soil than for sediment. Rate constants decreased with increasing Log K_{ow} (octanol-water partition coefficient)[50] (Figure S7.1) as expected when the diffusion through the UBL surrounding the SPME fiber is the rate limiting step.[25–30] Humic acids in solutions were therefore expected to enhance chemical release from the matrix increasing water capacity and speed-up mass transfer through the UBL as observed in other studies.[38–41,51] However, addition of the HA solution to the soil matrix was not found effective in the present experiment (Figures S5.2, S5.3, S5.4), . This observation may be related to the slow desorption from the added HA compared to the diffusion of the freely dissolved chemicals through the UBL.[26,52]

Relative standard deviation among independent replicate vials in DI-SPME sampling was on average 21% in sediments and 11% in soil samples attesting a good reproducibility of the method. However, these values are similar to other experiments for PCBs in sediments and soils performed with (non-automated) DI-SPME (< 10%)[5] and coated jars (< 24%)[15] suggesting only minor improvements were gained by operating DI-SPME in automated mode concerning measurement reproducibility with the current agitation possibilities. Furthermore, equilibrium conditions in soil samples were reached just by PCB 28 and 52 suggesting that the applicability of the method could be limited to less hydrophobic chemicals (e.g. Log $K_{ow} < 6$) in matrices poor in OC (e.g. < 1-2 %).

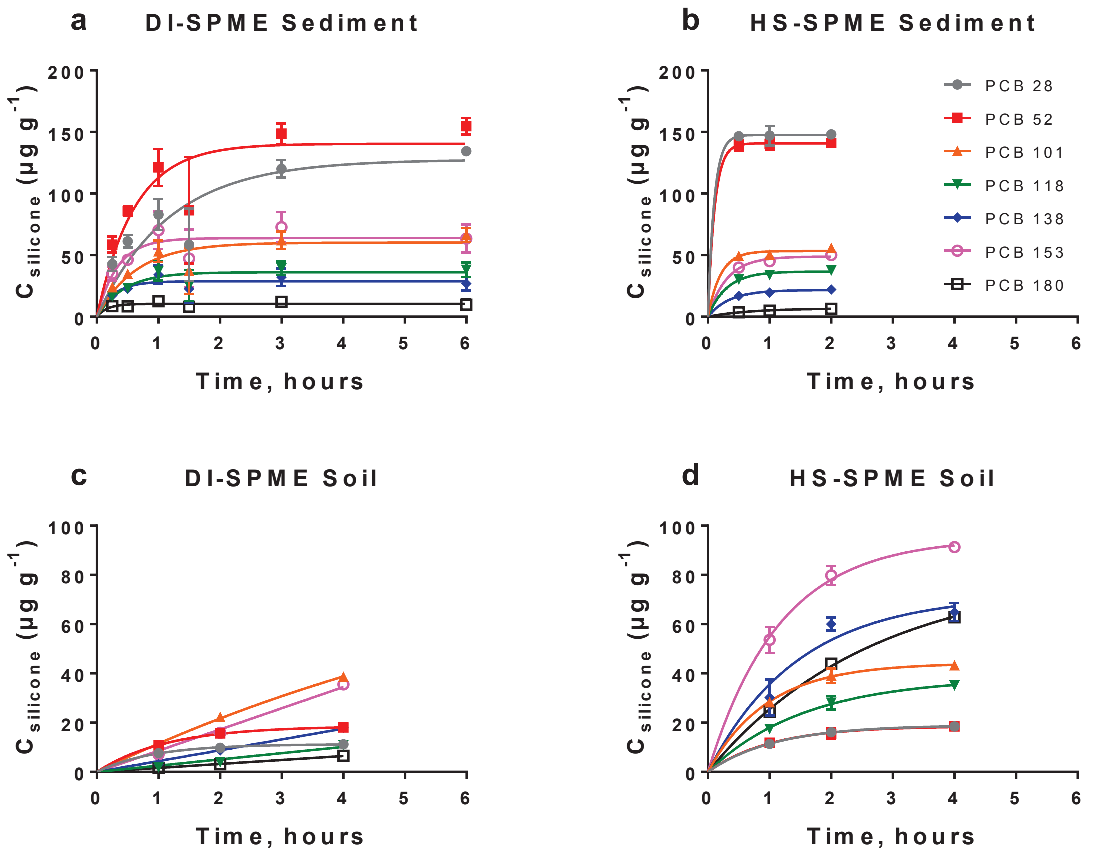

Figure 1. PCB sampling kinetics for sediment in DI-SPME (a) and in HS-SPME (b) and for soil in DI-SPME (c) and in HS-SPME (d) illustrated by the silicone concentrations (µg g^{-1}) plotted against the sampling time (hours). Average ± SEM, *n* = 3. For single congener graphs see S5, S6.

HS-SPME. For HS-SPME of sediments (Figure 1b, Figure S6.1) equilibrium was reached within 30 minutes for low chlorinated congeners (PCB 28 and 52) and within 2 hours for the more hydrophobic PCB 180. Sampling kinetics in HS-SPME for soil (Figure 1d, Figure S6.2) were also much faster compared to DI-SPME (Figure 1c, Figure S5.2) with t_{95} of 3-4 hours for PCB 28, 52, 101, 118, 138 153 and 8 hours for 180. The rate constant of PCB 101, for example, was enhanced by a factor of 9 (Tables S5.1, S6.1). This means that in these conditions the equilibration time can be reduced from ~ 1 day to about 3 hours. The congener-specific rate constants in sediment and soil samples varied up to a factor of 10 with faster kinetics in sediment samples. This seems most related to the better mixing of sediment suspension that continuously supplied the suspension/headspace interface with new sample,[15] compared to the dry soil samples that remained more stagnant. Further investigations are needed to elucidate the possibilities for speeding up sampling kinetics for soil samples by increasing the soil to air exchange area. Relative standard deviations among independent replicate vials was on average 9% both for sediments and soil samples showing an excellent reproducibility of the automated HS approach, in the same range as reported for non-automated methods.[15] HS-SPME also had the advantage of no fiber fouling and hence reduced carry over and elongated fiber life time. The lack of carryover is confirmed by clean blanks after HS-SPME measurements while after DI-SPME analyses blanks were sometimes contaminated by the target chemicals (in concentrations orders of magnitude lower than in the samples). Attention has to be paid by using DI-methods to the carryover effect if samples with very large variation in contamination level are analyzed in same sequence. Compared to other PCB measurements by HS-SPME with the same fiber phase and coating thicknesses at lower temperatures (35 °C),[15] sampling kinetic at 80 °C were much faster. Mäenpää et al (2011) reported equilibration times ranging from 0.3 to 5.7 days in sediments and from 8 days to 11 days in soil for PCBs. This suggests that HS-SPME at elevated temperature can extend applicability domain of the equilibrium HS-SPME analyses for HOCs with promising features to operate in automated mode (being faster, avoiding carryover and elongating coating lifetime). Furthermore, HS-SPME is suitable both for wet and dry matrices (e.g. building materials). The main disadvantages of HS-SPME are the need for heating up the sample which potentially can change the sample matrix and the intrinsic limitation of the method to analytes with a certain volatility.

Cross validation between DI-SPME and HS-SPME for C_{free} determination. $C_{silicone}$ concentrations were measured with both methods in sediment and soil samples extracted for 4 hours. Since in sediment samples different sampling times were performed for DI-SPME and HS-SPME temporal series (Figure 1), an independent experiment with 4 hour sampling by both approaches was performed. This time was sufficient for equilibrium sampling in sediment, which required 3 or 2 hours respectively for DI-SPME and HS-SPME while for soil the values were eventually corrected for dis-equilibrium (e.g. PCB 101 in DI-SPME) by equantio 9.

The two methods were generally in agreement (Figure 2) with no statistically significant differences (Student's t test) for all congeners in sediment samples or within a factor of 2.3 (PCB 28, $p = 0.02$; PCB 101, $p = 0.002$) for soil samples (Table S9.1). Although the differences observed were generally not statistically significant, the deviation from the 1:1 line appears with PCB concentrations generally lower in HS-SPME. This can be related to the potential fouling of the fiber in DI-SPME. This hypothesis is consistent with the strong positive correlation between the deviation from the 1:1 line observed (expressed ad ratios between DI-SPME and HS-SPME silicone concentrations) and the Log Kow of the chemicals ($R^2 = 0.89$, $p = 0.0000$). The good agreement between the two methods means the HS-SPME at 80 °C may be used for determining C_{free} reducing sampling time, increasing reproducibility and eliminating the disadvantages related to the direct immersion and potential fouling of the fiber. C_{free} were determined according to equation 2 for both approaches in sediment and soil sample (Table 2) and were strongly correlated ($C_{free\ (HS)} = 0.86\ C_{free\ (DI)} + 0.43$; $R^2 = 0.99$, $p = 0.000$) with slope of the regression curve close to 1 (0.86 ± 0.03) and intercept close to 0 (0.43 ± 5).

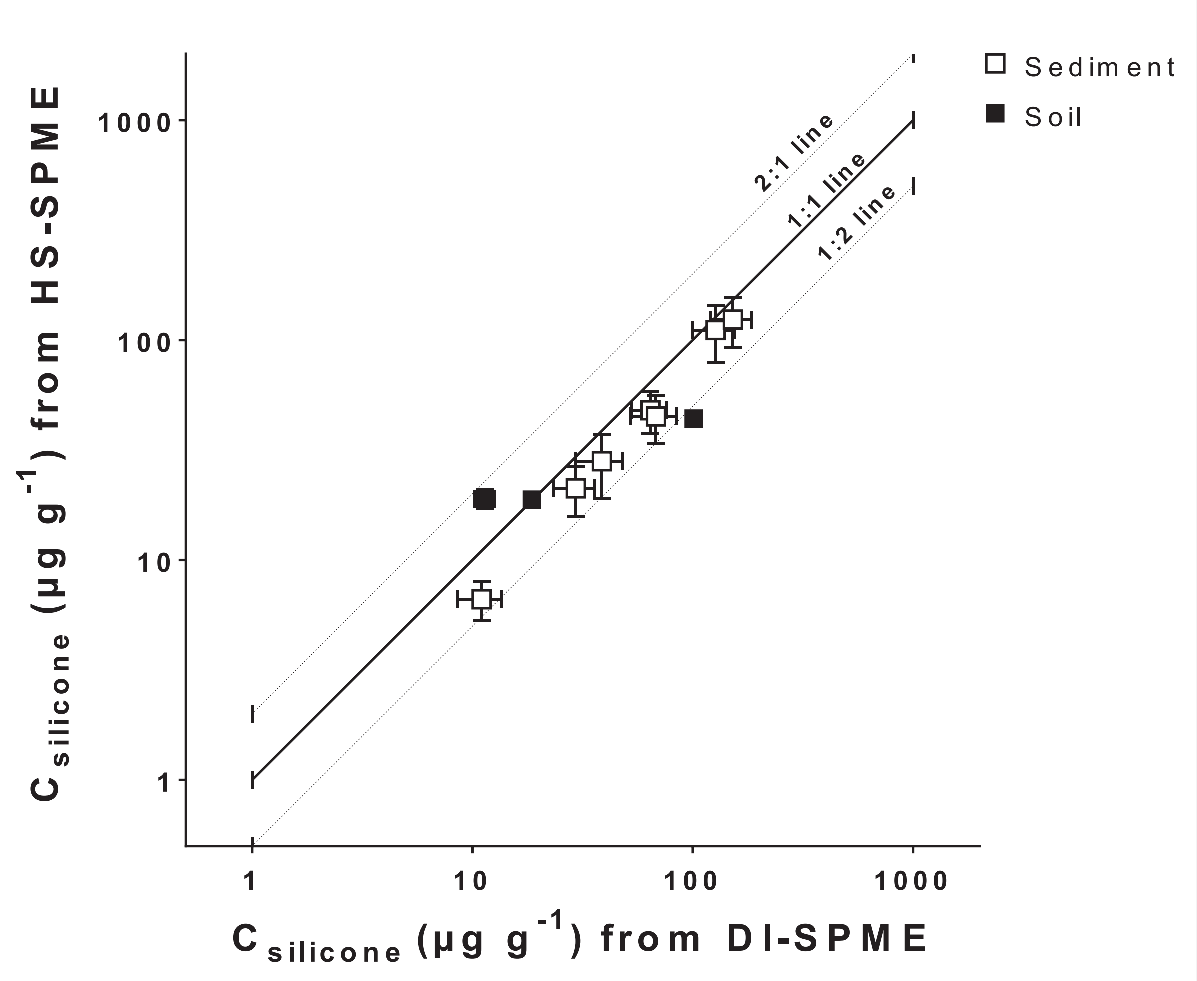

Figure 2. Silicone concentrations (µg g^{-1}) of all target chemicals measured with DI-SPME *vs.* HS-SPME in sediment and soil at equilibrium. Average ± CI, *n* = 3. Solid line: 1 to 1 line. Dashed line: factor of 2 deviation.

Table 2. Freely dissolved concentrations (C_{free}) in sediment and soil samples determined with DI-SPME and HS-SPME using the partitioning coefficient from Smedes et al (2009).[45] Average ± SD, *n* = 3.

Congener	C_{free} (ng L^{-1})			
	Sediments		Soil	
	DI-SPME	HS-SPME	DI-SPME	HS-SPME
PCB 28	375 (± 71.6)	328 (± 83.7)	33.6 (± 2.44)	56.0 (± 4.04)
PCB 52	240 (± 44.5)	197 (± 44.5)	29.4 (± 1.13)	29.8 (± 1.61)
PCB 101	33.7 (± 5.41)	25.2 (± 4.47)	53.2 (± 1.63)	23.1 (± 0.88)
PCB 118	14.7 (± 3.19)	10.7 (± 3.02)	Not determined	14.5 (± 0.55)
PCB 138	5.02 (± 0.93)	3.60 (± 0.83)	Not determined	11.8 (± 0.95)
PCB 153	13.0 (± 2.68)	8.58 (± 1.86)	Not determined	18.0 (± 0.28)
PCB 180	1.12 (± 0.22)	0.68 (± 0.12)	Not determined	8.25 (± 0.01)

C_{total} determination by DI-SPME and exhaustive extraction - validation. Total concentrations of PCBs in soil samples were determined by DI-SPME and ^{13}C labeled PCB congeners (equation l). The peak area ratios between ^{13}C labelled and ^{12}C native PCBs were determined after 2 and 14 days after spiking. Furthermore, data were compared to C_{total} measurements obtained in another laboratory by exhaustive extraction (EE) (see S1 for details) to validate the SPME approach for measurements of total PCB concentration. Generally, there was no significant difference (one-way

ANOVA) between total concentrations obtained by DI-SPME after 2, and 14 days after spiking and total concentrations obtained by exhaustive extractions in a different laboratory (PCB 52, 101, 118, 138, 153). For PCB 180 the difference was significant (ANOVA, Tuckey *post hoc* comparison, $p = 0.02$) between DI-SPME after 14 days and EE but within a factor of 1.3. PCB 28 concentrations determined by SPME were, on average, a factor of 2 higher in comparison to EE because PCB 31 (co-eluent of PCB 28)[54] was included in the EE calibration curve while only the labelled PCB 28 was used for SPME measurements. Since PCB 31 is actually present in soil,[37,38] the concentration measured by SPME are overestimated by using PCB 28 as only internal standard. The agreement between measurements at 2 and 14 days from spiking suggests that a brief equilibration time (2 days) can be used for determining $C_{total.}$ Similarly to our data, no differences were observed in K_{oc} values of PCB 153 measured by DI-SPME after 0 and 56 days from spiking in arable and forest soils.[22] Relative standard deviations in C_{total} measurements by SPME was on average 9%, even lower than EE (16%), proving an excellent reliability of the method despite the small mass of sample (0.5 g) used. In comparison to EE, the SPME approach presents several advantages in terms of time saving, solvent reduction and dangerous waste production, costs and safety for the operator.

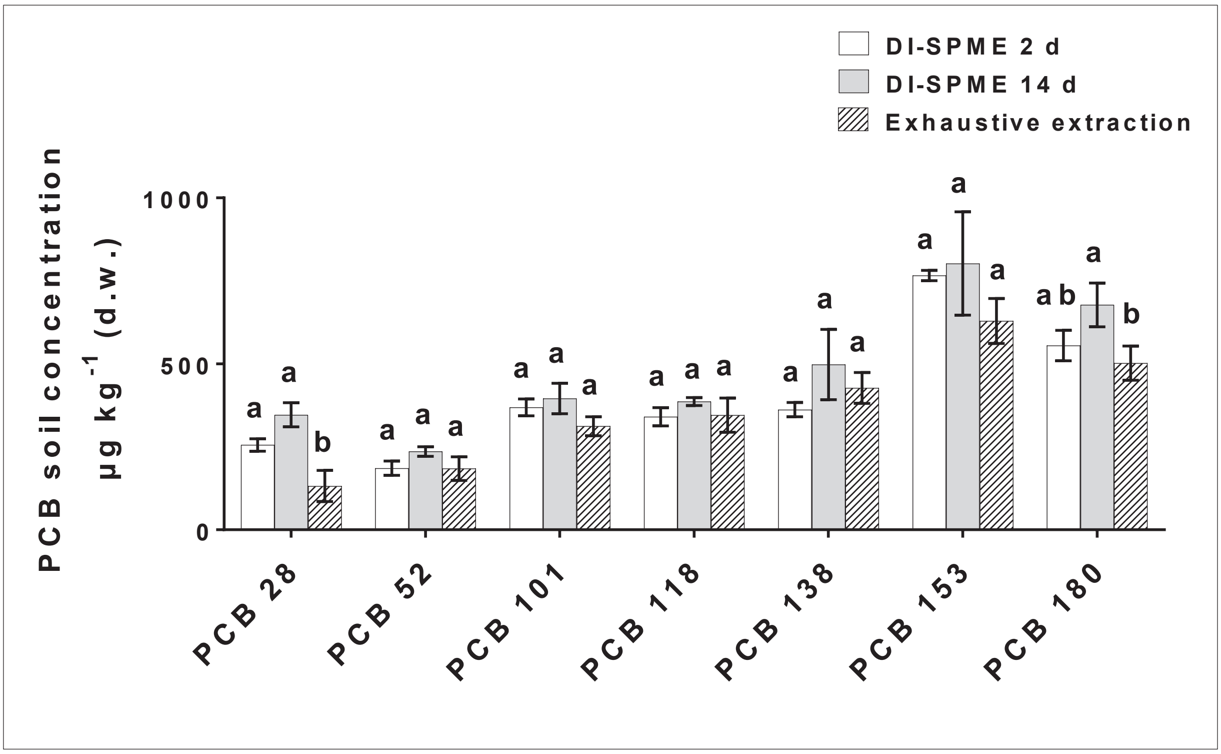

Figure 3. PCB total soil concentrations obtained by the new DI-SPME and spiked labelled standards after 2 and 14 days (d) from the spike, compared to total concentrations obtained by exhaustive extraction (EE). Average ± SD, *n* = 3. Statistically significant differences (ANOVA, α = 0.05, Tukey post hoc test) are indicated by different letters above bars.

Method application for measuring partitioning coefficients. K_d average values were calculated from C_{free} and C_{total} and normalized to the fraction of organic carbon (f_{oc}) to estimate K_{oc} values (equation 3 and 4) (Table S8.1). C_{total} in soil were taken from DI-SPME data after 14 days of equilibration from spiking. Since equilibrium C_{free} by DI-SPME in soil samples was not feasible for most PCB congeners (PCB 101, 118, 138, 153,180) and/or related rate constant were not determined by GraphPad fitting (Table S5.1.), C_{free} from HS-SPME (plateau values) were used to calculate K_d. However, whenever possible, C_{free} and C_{total} should be measured simultaneously.

An excellent positive correlation ($R^2 = 0.99$, $p < 0.0001$) was found between Log K_{ow}[50] and Log K_{oc} in soil: Log $K_{oc} = (0.67 \pm 0.03)$ Log $K_{ow} + (1.80 \pm 0.20)$. Even in sediments, where C_{total} were measured in an external laboratory (S1) and C_{free} obtained as average values ($n = 6$) of the HS and DI-SPME measurements (samples extracted for 4 hours), Log K_{ow} correlates well ($R^2 = 0.90$; $p = 0.001$) with Log K_{oc}: (0.86 ± 0.13) Log $K_{ow} + (0.75 \pm 0.83)$.

The method presented here allows for K_d determination by measuring both C_{free} and C_{total} (potentially in the same sample analysis) while avoiding the experimental artefacts related to the incomplete physical separation of matrix and water within batch tests. The so-called "third phase effect"[55,56] due to the remaining DOC/colloids in the water fraction that can lead to significant underestimations of the partition coefficient[57] with an extent depending on the liquid to solid ratio[58,59] is avoided with the new approach. The new approach can conjugate the regulatory requirement for C_{total} measurements with the emerging need to measure C_{free} to account for chemical bioavailability and obtain more realistic risk assessment.

Relevance and implications. HS-SPME at elevated temperature is a new, practical and valid alternative to DI-SPME and other direct immersion sampling methods for determination of C_{free} of HOCs tested in the present study in both carbon rich and carbon poor matrices. Importantly, HS-SPME (1) is applicable to a wide range of samples, (2) circumvents polymer fouling and breaking of fiber needles and (3) is amendable to automatization which can significantly increase sample throughput. Faster kinetics are obtained by the more efficient release of chemicals from the contaminated matrix, the higher concentration in the headspace and the enhanced diffusion coefficients.[20] The equilibrium concentration in the polymer will be the same for HS-SPME and

DI-SPME when the temperature effect is very similar on matrix-air and air-polymer partitioning, which implies a largely temperature independent organic carbon-polymer partitioning. The successful cross validation in the present study supports that this assumption was valid for the tested analytes and matrixes.

With only one measurement method, both C_{free} and C_{total} can be measured allowing the estimation of sample and analyte specific K_d values. Even when equilibrium sampling was relatively long (e.g. 8 hours for PCB 180 in soil samples), the approach proposed is still fast compared to traditional K_d determination methods. Finally, K_d determination by SPME can reduce potential artefacts due to the filtration and separation between aqueous and solid matrix, especially when relatively hydrophobic chemicals are measured.

Overall, both approaches to speed up the SPME sampling kinetics were found efficient and sound but require also further research and testing. The sampling kinetics of DI-SPME can likely be further improved using more efficient agitation modes, whereas a short rinsing step in pure water might reduce the observed carry over. The further development and final validation of HS-SPME at elevated temperatures requires some additional dedicated experiments to determine the temperature dependence of the PCB partitioning between natural organic carbon and the PDMS coating.

SUPPORTING INFORMATION

Sediment and soil characterization (OC content, PCB concentrations) (S1). Log K_{ow} and Log $K_{silicone\text{-}water}$ partition coefficients (S2). QA/QC (S3). Experiments at different L:S ratios (S4). Uptake kinetics and rate constants (S5, S6, S7). Average Log K_{oc} for sediment and soil samples (S8).

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Supporting information for

Accelerated equilibrium sampling of hydrophobic organic chemicals in solid matrices – automated SPME with reduced equilibration times

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Table of content

S1. Sediment and soil characterization

S2. Partition coefficients of the target chemicals

S3. Quality assurance/Quality control (QA/QC)

S4. Experiments at different liquid to solid ratio (L:S)

S5. PCB uptake kinetics in DI-SPME

S6. PCB uptake kinetics in HS-SPME

S7. Rate constants *vs.* Log Kow values

S8. Log K_{oc} in sediment and soil samples

S9. Statistical tests

References

S1. Sediment and soil characterization

In sediments (Table S1.1) total solids were determined by Eurofins A/S using the method DS 204 with a method detection limit (MDL) of 0.05%, total organic carbon (TOC) was determined by Eurofins A/S with the method DS/EN 13137 Dumas (TCD) with a MDL of 500 mg kg^{-1} (d.w.) while PCB concentrations were measured by Eurofins A/S with method M 2060 GC-MS with a MDL of 0.001 mg kg^{-1} (d.w.) for all congeners. In soil (Table S1.2) the organic carbon content was determined as reported in.[1] For PCB determination in soil by exhaustive extraction, soil samples (~ 5 g x 3 replicates) were extracted with 100 mL of cyclohexane by sonication[2], 2 mL of the extract were cleaned-up[3] and concentrated to ~ 100 µL before GC-MS analysis.

Table S1.1. Sediment characterization.

Sediment characterization	
Total solids	54%
TOC	3.6% (d.w.)
PCB 28	4.0 (mg kg^{-1}) (d.w.)
PCB 52	4.4 (mg kg^{-1}) (d.w.)
PCB 101	2.1 (mg kg^{-1}) (d.w.)
PCB 118	1.6 (mg kg^{-1}) (d.w.)
PCB 138	1.3 (mg kg^{-1}) (d.w.)
PCB 153	1.2 (mg kg^{-1}) (d.w.)
PCB 180	0.3 (mg kg^{-1}) (d.w.)
ΣPCBs	15 (mg kg^{-1}) (d.w.)

Table S1.2. Soil characterization.

Soil characterization	
TOC	1.5 (± 0.2) % (d.w.)
PCB 28	132 (± 47) (µg kg $^{-1}$) (d.w.)
PCB 52	184 (± 36) (µg kg^{-1}) (d.w.)
PCB 101	312 (± 028) (µg kg^{-1}) (d.w.)
PCB 118	345 (± 52) (µg kg^{-1}) (d.w.)
PCB 138	427 (± 47) (µg kg^{-1}) (d.w.)
PCB 153	629 (± 68) (µg kg^{-1}) (d.w.)
PCB 180	502 (± 51) (µg kg^{-1}) (d.w.)
ΣPCBs	2532 (± 230) (µg kg^{-1}) (d.w.)

S2. Partition coefficients of the target chemicals

Table S2.1. Octanol-water (Log K_{OW}) and silicone-water (Log $K_{silicone\text{-}water}$) partition coefficients of the target chemicals.

Congener	Log K_{OW}[4]	Log $K_{silicone\text{-}water}$[5]
PCB 28	5.67	5.53
PCB 52	5.84	5.8
PCB 101	6.38	6.28
PCB 118	6.74	6.42
PCB 138	6.83	6.77
PCB 153	6.92	6.72
PCB 180	7.36	6.99

S3. Quality assurance/Quality control (QA/QC)

QA/QC were performed by 1) setting a maximum deviation of 15% from the ratios expected between quantifier and qualifier ions (Table S3.1), 2) laboratory blanks, 3) preparation of the samples in duplicates or triplicates. PCB signal in blanks was generally 1-2 orders of magnitude lower compared to samples. MDL (Table S3.2) was calculated multiplying the standard deviation of 7 replicate measurements of the lowest calibration point by the Student's t value (1.943 for p = 0.05 and df = 6).[6]

Table S3.1. Quantifier and qualifier ions for each congener.

Congener	Quantifier ion (m/z)	Qualifier ion (m/z)
PCB 28	256	258
PCB 52	290	292
PCB 101	326	328
PCB 118	326	328
PCB 138	360	362
PCB 153	360	362
PCB 180	394	396

Table S3.2. MDL (pg L^{-1}) of different congeners.

Congener	MDL (pg L^{-1})
PCB 28	169
PCB 52	241
PCB 101	27.9
PCB 118	25.9

PCB 138	11.2
PCB 153	12.8
PCB 180	11.4

S4. Experiments at different liquid to solid ratio (L:S)

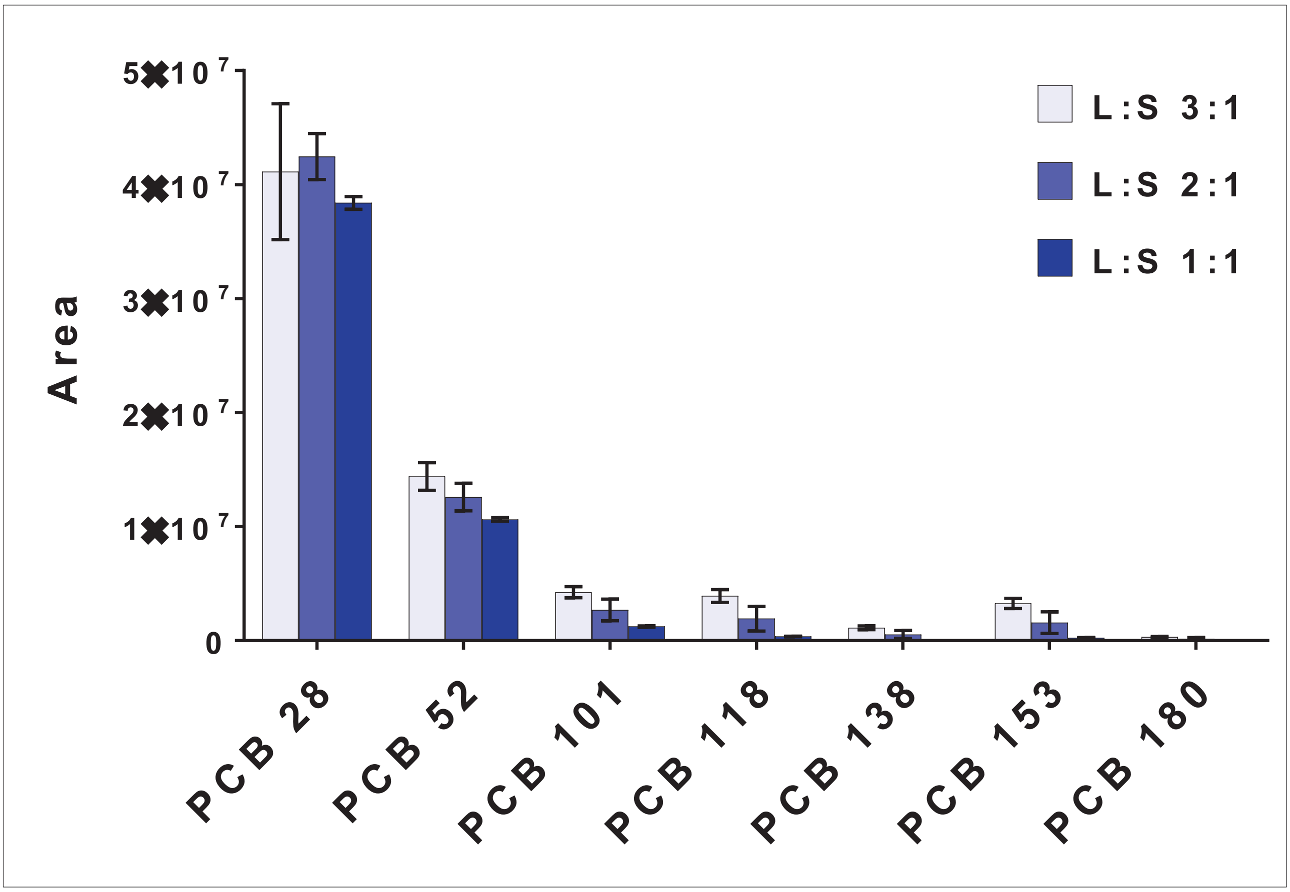

Figure S4.1. PCB peak areas at different liquid to solid (L:S) ratios for an extraction time of 30 minutes in sediment samples. The error bars show the standard deviation of mean of 3 replicates.

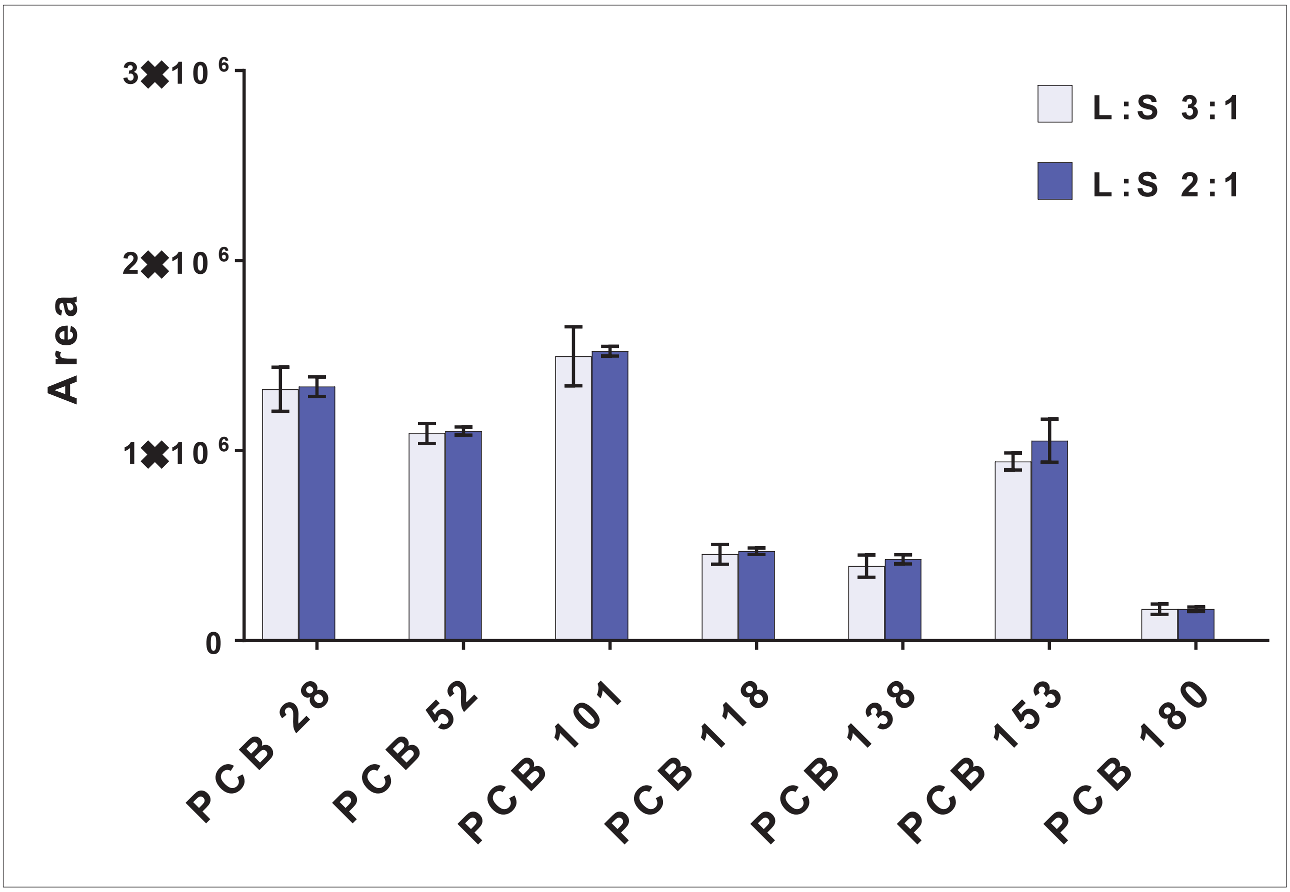

Figure S4.2. PCB peak areas at different liquid to solid (L:S) ratios for an extraction time 1 hour in soil samples. The error bars show the standard deviation of mean of 3 replicates.

L/S ratio experiments. In sediment samples (Figures S4.1) no significant differences (ANOVA, $\alpha = 0.05$) in sampling rate were observed for low chlorinated congeners (PCB 28 and 52) while faster kinetics were observed for the other by increasing L:S ratios with and extend increasing with their hydrophobicity (up to an order of magnitude for PCB 180). For soil samples (Figures S4.2) no significant differences (Student's t test, $\alpha = 0.05$) were observed for all congeners. The differences observed in sediments may be related to the reduction of the viscosity of the medium that facilitates the mixing and speed up the kinetics. On the contrary, in soil samples where the mixing is facilitated by low viscosity of the medium, the L:S ratio does not affect the kinetics. The L:S 3:1 was therefore selected for the next experiments.

S5. PCB uptake kinetics in DI-SPME

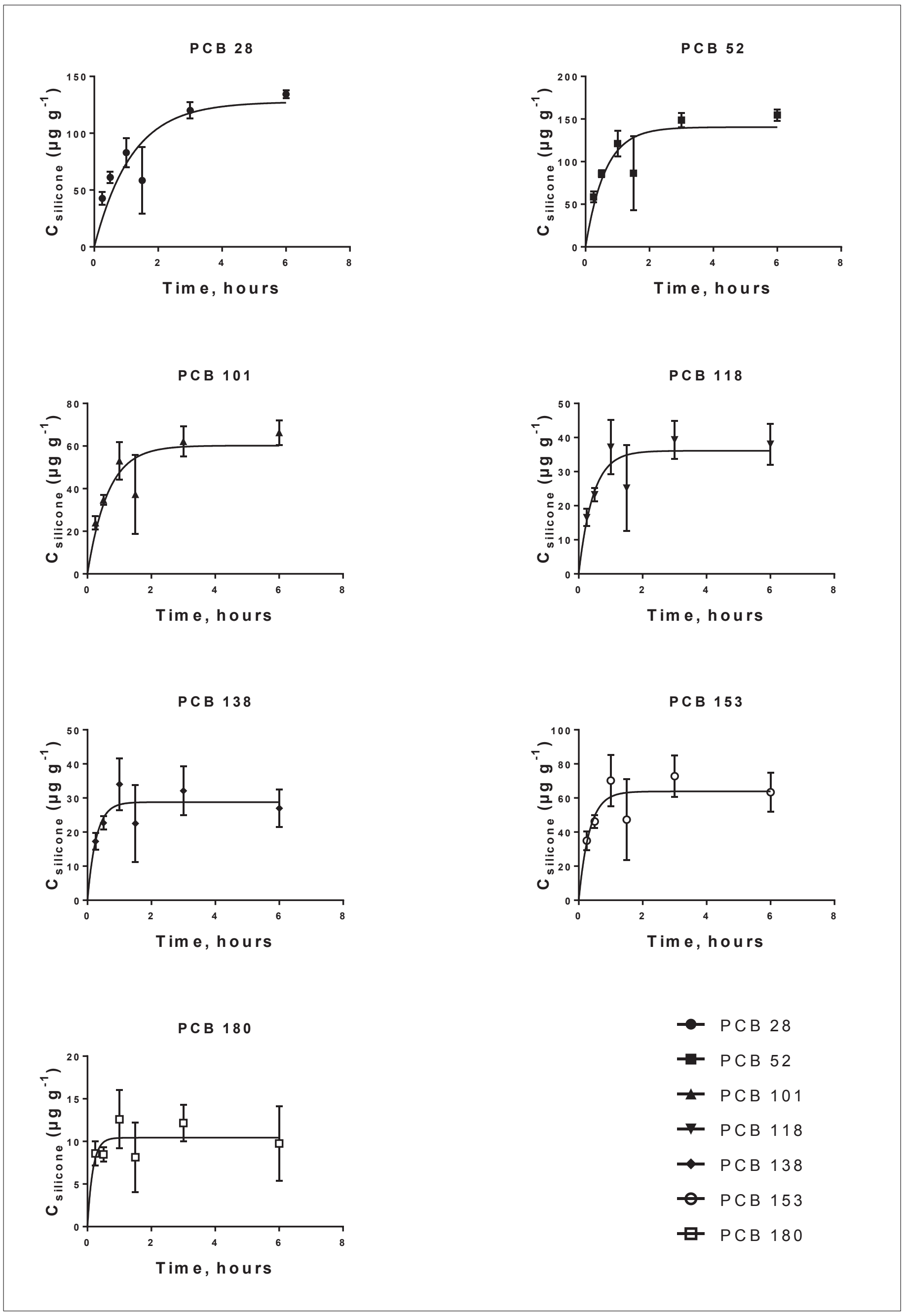

Figure S5.1. PCB uptake kinetics in DI-SPME illustrated by the silicone concentrations (µg g^{-1}) plotted against the extraction time (hours) for sediment samples. The error bars show the standard error of mean of 3 replicates. Please note the different scales used for different congeners.

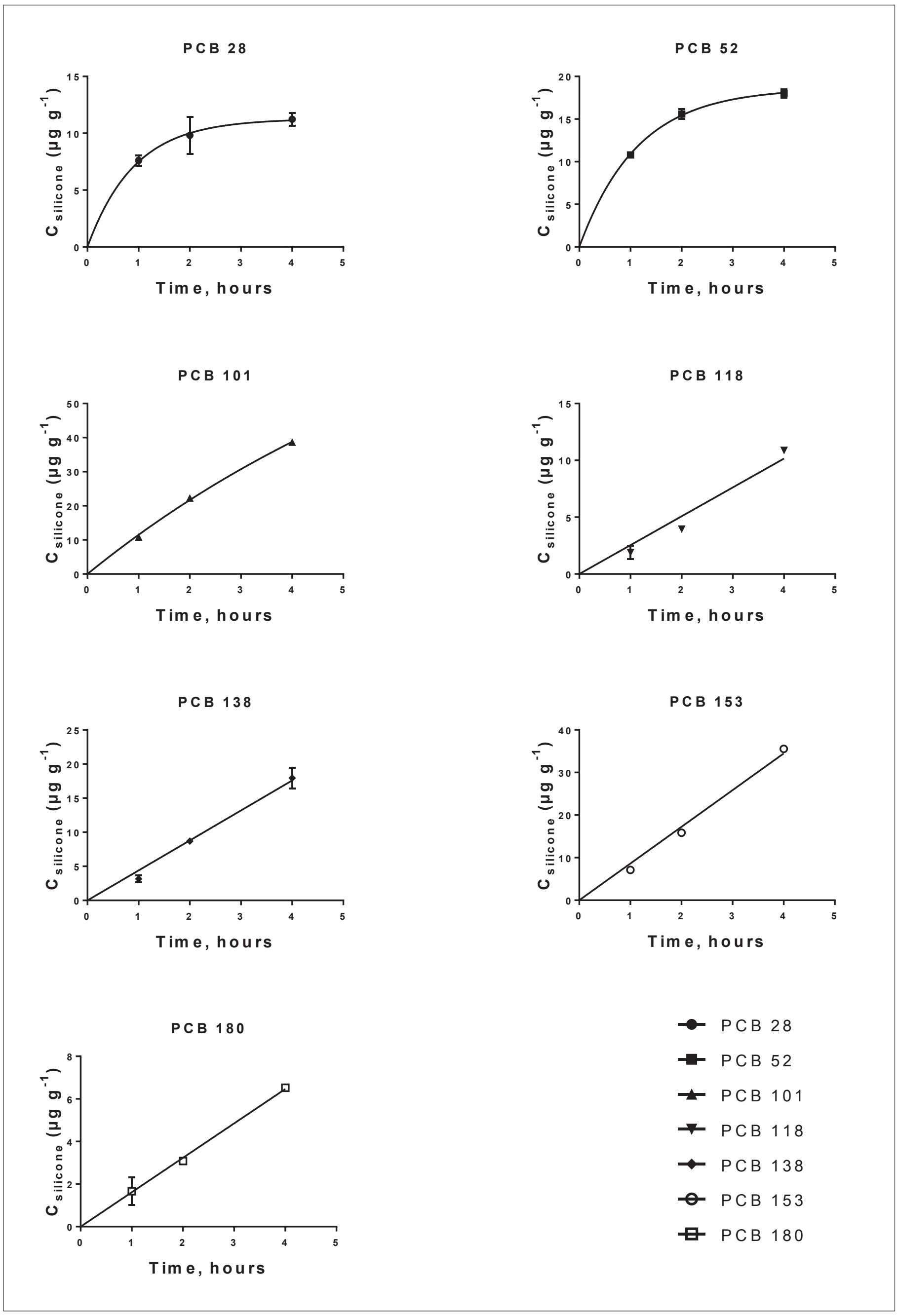

Figure S5.2. PCB uptake kinetics in DI-SPME illustrated by the silicone concentrations (µg g^{-1}) plotted against the extraction time (hours) for soil samples. The error bars show the standard error of mean of 2 replicates. Please note the different scales used for different congeners.

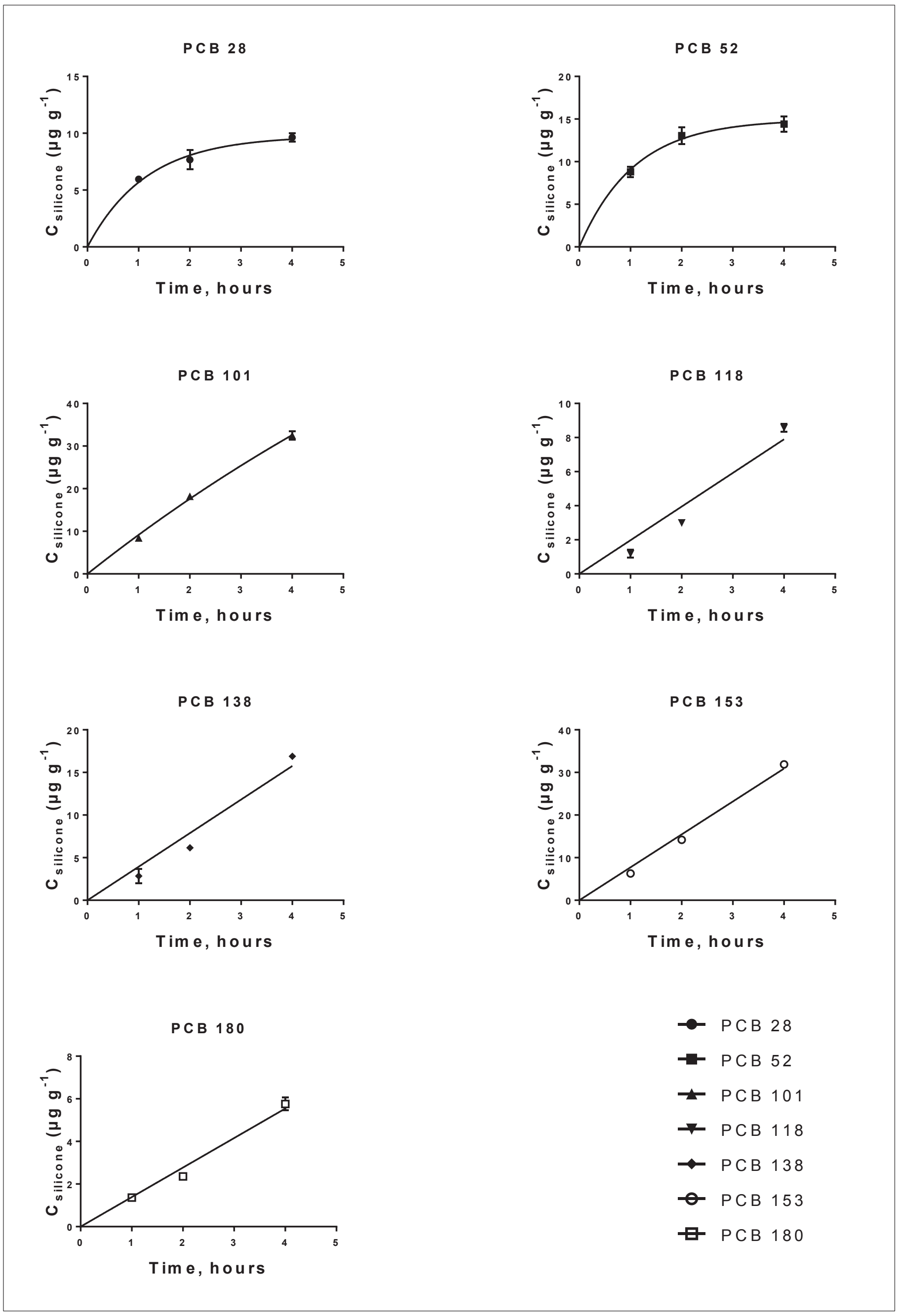

Figure S5.3. PCB uptake kinetics in DI-SPME illustrated by the silicone concentrations (µg g^{-1}) plotted against the extraction time (hours) for soil samples treated with HA. The error bars show the standard error of mean of 2 replicates. Please note the different scales used for different congeners.

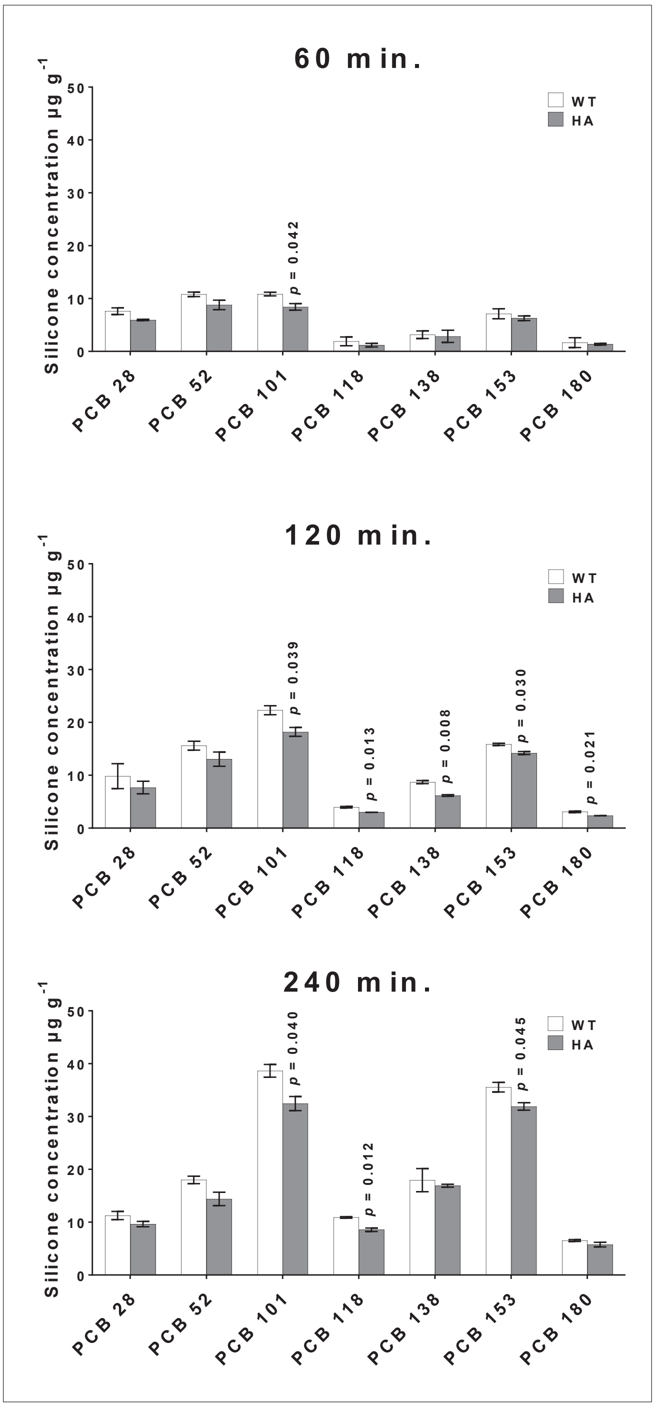

Figure S5.4. PCB silicone concentrations in DI-SPME for samples treated with water (WT) vs. humic acid (HA) with extraction times of 60, 120 and 240 minutes. For differences statistically significant (Student's t test, $\alpha = 0.05$) *p* values are reported.

Table S5.1. PCB rate constants (mean and standard error) in DI-SPME calculated by fitting to a first-order one-compartment model the data for sediment and soil samples.

Congener	Rate constant k (h^{-1})		
	Sediments	Soil	Soil + HA
PCB 28	1.13 (± 0.17)	1.09 (± 0.32)	0.87 (± 0.17)
PCB 52	1.71 (± 0.20)	0.88 (± 0.07)	0.93 (± 0.18)
PCB 101	1.66 (± 0.29)	0.12 (± 0.03)	0.08 (± 0.04)
PCB 118	2.10 (± 0.55)	Not reliable	Not reliable
PCB 138	3.11 (± 1.14)	Not reliable	Not reliable
PCB 153	2.60 (± 0.78)	Not reliable	Not reliable
PCB 180	4.45 (± 2.50)	Not reliable	Not reliable

Table S5.2. PCB plateau freely dissolved concentration (mean and standard deviation) in DI-SPME calculated by fitting to a first-order one-compartment model the data for sediment and soil samples.

Congener	Plateau concentration (ng L^{-1})		
	Sediments	Soil	Soil + HA
PCB 28	422.96 (± 37.15)	33.27 (± 4.09)	28.85 (± 2.81)
PCB 52	146.60 (± 9.11)	29.59 (± 1.19)	23.70 (± 2.12)
PCB 101	20.99 (± 1.94)	53.38 (± 17.00)	61.85 (± 40.69)
PCB 118	16.94 (± 2.14)	Not reliable	Not reliable
PCB 138	4.04 (± 0.61)	Not reliable	Not reliable
PCB 153	8.96 (± 1.20)	Not reliable	Not reliable
PCB 180	0.91 (± 0.18)	Not reliable	Not reliable

S6. PCB uptake kinetics in HS-SPME

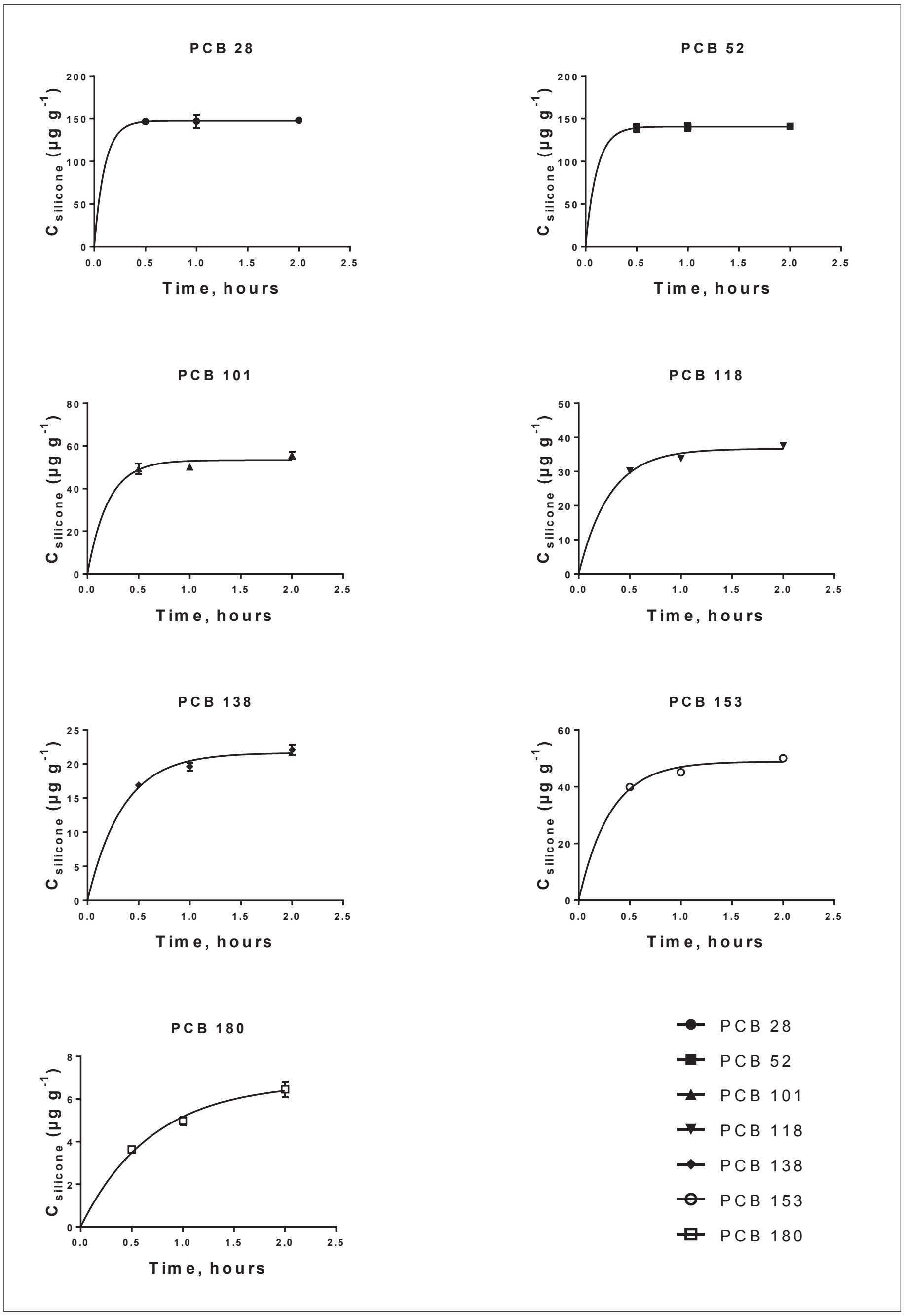

Figure S6.1. PCB uptake kinetics in HS-SPME illustrated by the silicone concentrations (µg g^{-1}) plotted against the extraction time (hours) for sediment samples. The error bars show the standard error of mean of 3 replicates. Please note the different scales used for different congeners.

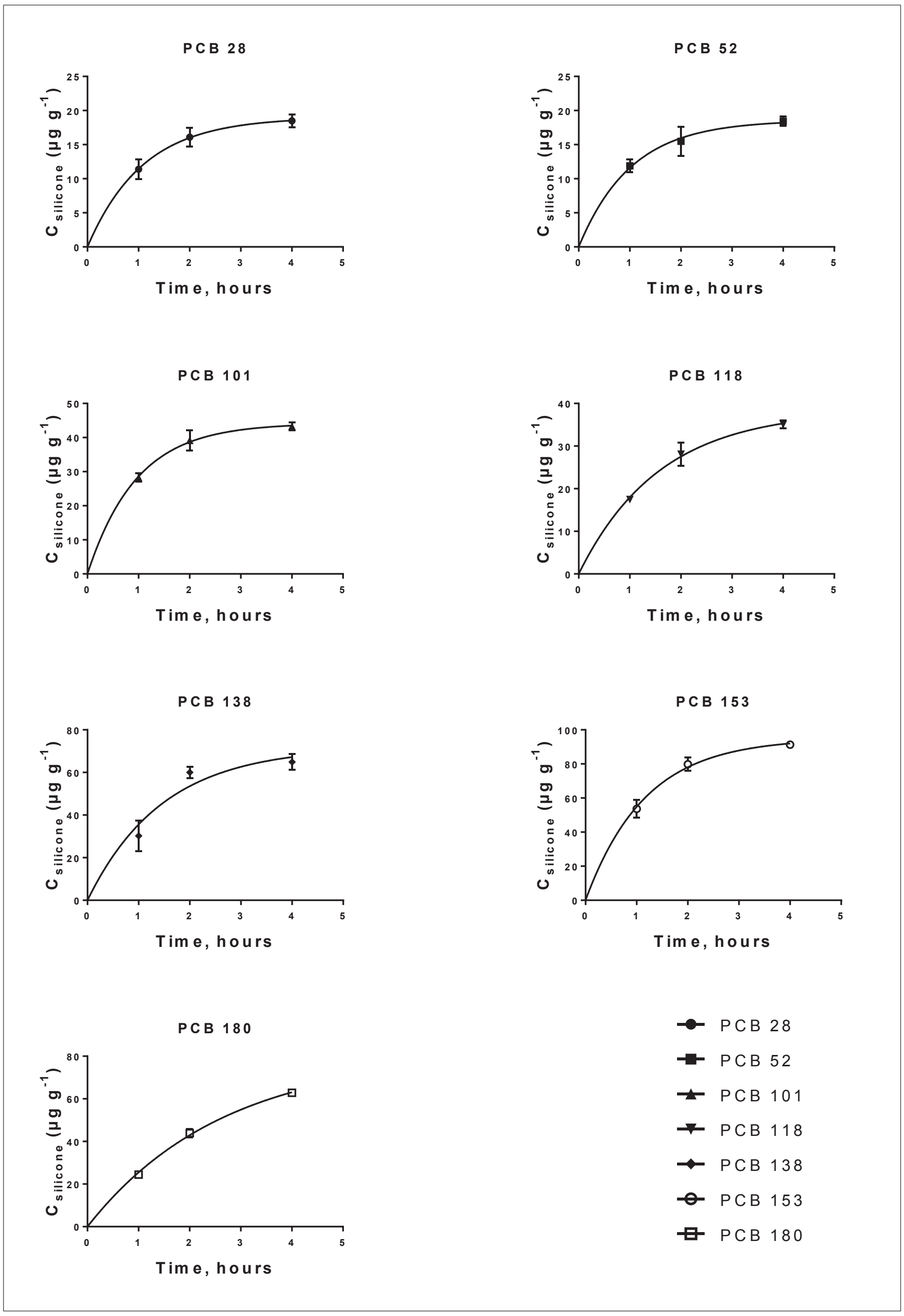

Figure S6.2. PCB uptake kinetics in HS-SPME illustrated by the silicone concentrations (µg g^{-1}) plotted against the extraction time (hours) for soil samples. The error bars show the standard error of mean of 2 replicates. Please note the different scales used for different congeners.

Table S6.1. PCB rate constants (mean and standard error) in HS-SPME calculated by fitting to a first-order one-compartment model the data for sediment and soil samples.

Congener	Rate constant k (h^{-1})	
	Sediments	Soil
PCB 28	9.79 (± 11.10)	0.92 (± 0.20)
PCB 52	9.04 (± 5.64)	0.98 (± 0.24)
PCB 101	4.95 (± 1.22)	1.04 (± 0.15)
PCB 118	3.31 (± 0.32)	0.63 (± 0.11)
PCB 138	2.89 (± 0.34)	0.68 (± 0.24)
PCB 153	1.44 (± 0.32)	0.86 (± 0.12)
PCB 180	3.23 (± 0.22)	0.38 (± 0.04)

Table S6.2. PCB plateau freely dissolved concentration (mean and standard deviation) in HS-SPME calculated by fitting to a first-order one-compartment model the data for sediment and soil samples.

Congener	Plateau concentration (ng L^{-1})	
	Sediments	Soil
PCB 28	491.76 (± 20.49)	56.12 (± 5.72)
PCB 52	137.75 (± 4.25)	29.45 (± 3.31)
PCB 101	17.50 (± 0.94)	23.19 (± 1.43)
PCB 118	15.82 (± 0.56)	14.59 (± 1.48)
PCB 138	2.78 (± 0.14)	12.21 (± 2.43)
PCB 153	6.26 (± 0.23)	18.11 (± 1.24)
PCB 180	0.54 (± 0.06)	8.28 (± 0.72)

S7. Rate constants *vs.* Log K_{ow} values

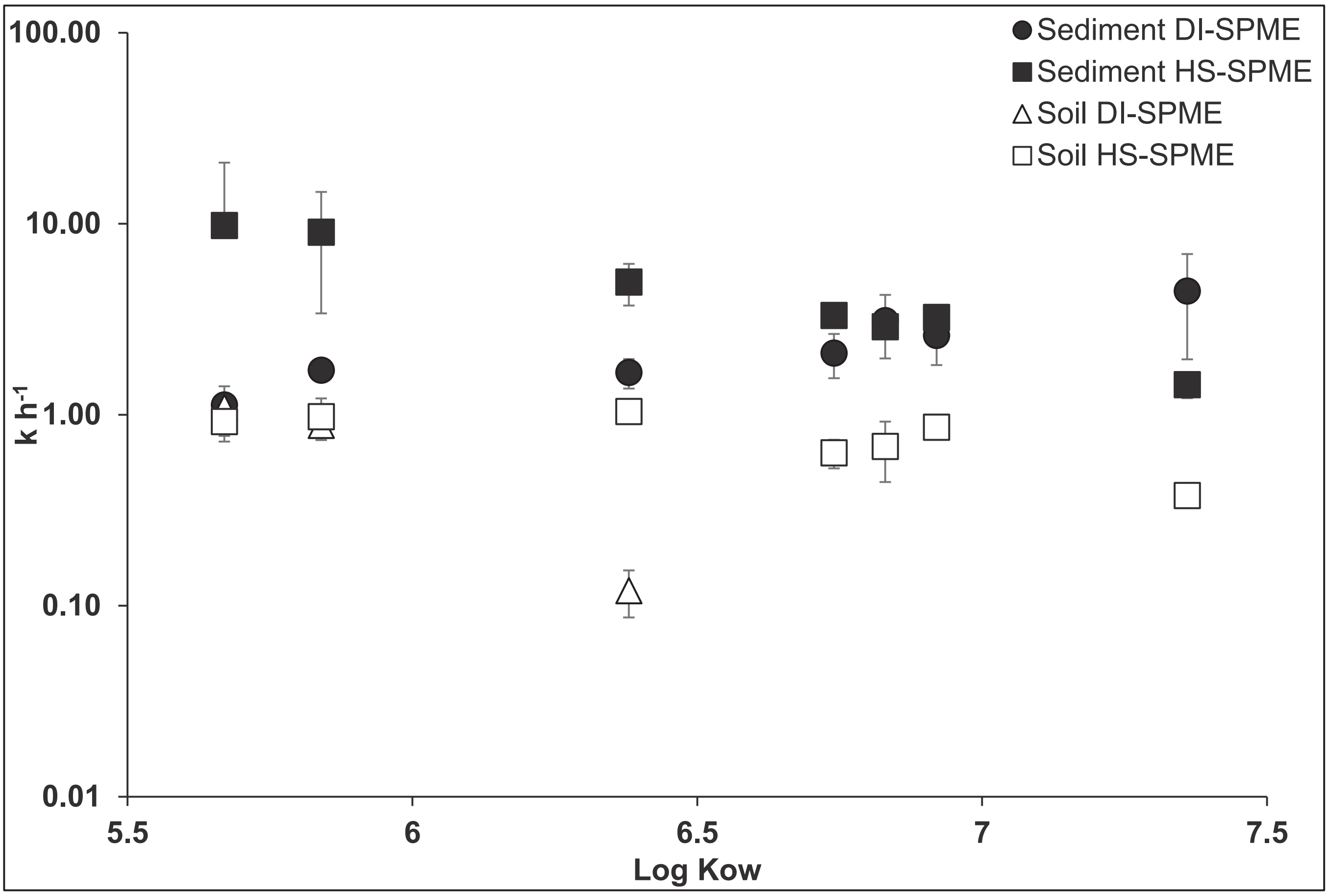

Figure S7.1. Rate constants (h^{-1}) *vs.* Log K_{ow}[4] of the target analytes in sediments and soil. The error bars show the standard error of mean of three or two replicates. In soil samples just PCB 28, 52, 101 and 138 are depicted for DI-SPME because for the other PCBs the model is not able to predict reliable k values.

S8. Log K_{oc} in sediment and soil samples

Table S8.1. Average Log K_{oc} for sediment and soil samples.

Chemicals	Log K_{oc}	
	Sediment	Soil
PCB 28	5.50	5.61
PCB 52	5.75	5.73
PCB 101	6.30	6.06
PCB 118	6.54	6.25
PCB 138	6.92	6.43
PCB 153	6.49	6.47
PCB 180	6.92	6.74

S9. Statistical tests

Table S9.1. Student's t test (α = 0.05) *p* values for DI-SPME and HS-SPME cross validation.

Chemicals	*p* values	
	Sediment	Soil
PCB 28	0.840	0.022
PCB 52	0.126	0.680
PCB 101	0.229	0.002
PCB 118	0.106	-
PCB 138	0.393	-
PCB 153	0.301	-
PCB 180	0.345	-

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