# Sampling Medium Side Resistance to Uptake of Semi-volatile Organic Compounds in Passive Air Samplers

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# Determination of PSM-air partition coefficients and sorption enthalpies of PCB congeners using poly-parameter linear free energy relationships

Poly-parameter linear free energy relationships (pp-LFERs) are available for XAD-air and PUF-air partition coefficients ( $K_{XAD/A}$  and  $K_{PUF/A}$ ).<sup>1,2</sup> Hayward et al. (1) estimated  $K_{XAD/A}$  and  $K_{PUF/A}$  for individual PCB congeners using these pp-LFERs and solute descriptors reported by Abraham et al..<sup>3</sup> Recently, van Noort et al.<sup>4</sup> showed the PCB solute descriptors from ref. (3) work poorly for highly ortho-chlorinated PCBs, making it is necessary to update the estimation of partition coefficients using the pp-LFERs and the new solute descriptors. <sup>4</sup> To calculate  $K_{XAD/A}$  at 20 °C, the pp-LFER:

$$\log K_{\text{XAD/A}} (20 \text{ °C}) = 0.45 \text{A} + 0.78 \text{L} - 0.37 \text{E} + 1.96$$
 (Eq. S1)

by Hayward et al.<sup>1</sup> was used. From  $K_{XAD/A}$  at 20 °C,  $K_{XAD/A}$  at other temperatures can also be derived using the van't Hoff equation:

$$\log \frac{K(T_1)}{K(T_2)} = -\frac{\Delta H_s}{2.303R} (\frac{1}{T_1} - \frac{1}{T_2})$$
(Eq. S2)

The sorption enthalpies ( $\Delta H_{S,XAD}$  in J/mol) can be estimated by another pp-LFER<sup>1</sup>:

$$\Delta H_{\text{s. XAD}}$$
 (J/mol) = (-17.5A - 2.36L + 2.44E - 27.3) · 1000 (Eq. S3)

The  $K'_{PUF/A}$  was first calculated using the pp-LFERs reported by Kamprad and Goss<sup>2</sup>:

$$K'_{PUF/A}(15^{\circ}C) = 3.66A + 1.69S + 0.71L16 + 0.36V - 0.15$$
 (Eq. S4)

Note that  $K'_{PUF/A}$  has units of cm<sup>3</sup>/g.  $K'_{PUF/A}$  (15 °C) was adjusted to 20 °C using the van't Hoff equation and sorption enthalpies ( $\Delta H_{S, PUF}$  in J/mol) calculated using <sup>2</sup>:

$$\Delta H_{\rm S, PHF} (\rm J/mol) = (-46.6A - 4.3L - 12.8V - 17.6S + 2.7) \cdot 1000$$
 (Eq. S5)

Then,  $K'_{PUF/A}$  (20 °C) was converted to unitless  $K_{PUF/A}$  (20 °C) using a PUF density of 0.02 g/cm<sup>3</sup>. K<sub>XAD/A</sub> and  $K_{PUF/A}$  at 20 °C are listed in Table S1 and Table S2.

PCB Congener	$\Delta H_{\rm S, XAD}$	log K <sub>XAD/A</sub> (20°C)	PCB Congener	$\Delta H_{\rm S, XAD}$	log K <sub>XAD/A</sub> (20°C)
IUPAC#	J/mol	(-)	IUPAC#	J/mol	(-)
1	-39289	6.57	43	-42405	7.79
2	-40313	6.89	44	-42405	7.79
3	-40313	6.89	45	-41475	7.50
4	-39682	6.77	46	-41475	7.50
5	-40691	7.09	47	-42405	7.79
6	-40691	7.09	48	-42405	7.79
7	-40691	7.09	49	-42405	7.79
8	-40691	7.09	50	-41475	7.50
9	-40691	7.09	51	-41475	7.50
10	-39682	6.77	52	-42405	7.79
11	-41738	7.42	53	-41475	7.50
12	-41738	7.42	54	-40529	7.20
13	-41738	7.42	55	-43496	8.13
14	-41738	7.42	56	-43496	8.13
15	-41738	7.42	57	-43496	8.13
16	-41043	7.28	58	-43496	8.13
17	-41043	7.28	59	-42405	7.79
18	-41043	7.28	60	-43496	8.13
19	-40132	7.00	61	-43496	8.13
20	-42093	7.61	62	-42405	7.79
21	-42093	7.61	63	-43496	8.13
22	-42093	7.61	64	-42405	7.79
23	-42093	7.61	65	-42405	7.79
24	-41043	7.28	66	-43496	8.13
25	-42093	7.61	67	-43496	8.13
26	-42093	7.61	68	-43496	8.13
27	-41043	7.28	69	-42405	7.79
28	-42093	7.61	70	-43496	8.13
29	-42093	7.61	71	-42405	7.79
30	-41043	7.28	72	-43496	8.13
31	-42093	7.61	73	-42405	7.79
32	-41043	7.28	74	-43496	8.13
33	-42093	7.61	75	-42405	7.79
34	-42093	7.61	76	-43496	8.13
35	-43162	7.95	77	-44587	8.48
36	-43162	7.95	78	-44587	8.48
37	-43162	7.95	79	-44587	8.48
38	-43162	7.95	80	-44587	8.48
39	-43162	7.95	81	-44587	8.48
40	-42405	7.79	82	-43766	8.30
41	-42405	7.79	83	-43766	8.30
42	-42405	7.79	84	-42817	8.01

**Table S1** XAD-air partition coefficients ( $K_{XAD/A}$ ) and sorption enthalpies ( $\Delta H_{S, XAD}$ , J/mol) for PCBs

PCB Congener	$\Delta H_{ m S, XAD}$	log K <sub>XAD/A</sub> (20°C)	PCB Congener	$\Delta H_{\rm S, XAD}$	log K <sub>XAD/A</sub> (20°C)
IUPAC#	J/mol	(-)	IUPAC#	J/mol	(-)
85	-43766	8.30	127	-46011	9.00
86	-43766	8.30	128	-45127	8.81
87	-43766	8.30	129	-45127	8.81
88	-42817	8.01	130	-45127	8.81
89	-42817	8.01	131	-44160	8.52
90	-43766	8.30	132	-44160	8.52
91	-42817	8.01	133	-45127	8.81
92	-43766	8.30	134	-44160	8.52
93	-42817	8.01	135	-44160	8.52
94	-42817	8.01	136	-43133	8.20
95	-42817	8.01	137	-45127	8.81
96	-41831	7.70	138	-45127	8.81
97	-43766	8.30	139	-44160	8.52
98	-42817	8.01	140	-44160	8.52
99	-43766	8.30	141	-45127	8.81
100	-42817	8.01	142	-44160	8.52
101	-43766	8.30	143	-44160	8.52
102	-42817	8.01	144	-44160	8.52
103	-42817	8.01	145	-43133	8.20
104	-41831	7.70	146	-45127	8.81
105	-44898	8.65	147	-44160	8.52
106	-44898	8.65	148	-44160	8.52
107	-44898	8.65	149	-44160	8.52
108	-44898	8.65	150	-43133	8.20
109	-43766	8.30	151	-44160	8.52
110	-43766	8.30	152	-43133	8.20
111	-44898	8.65	153	-45127	8.81
112	-43766	8.30	154	-44160	8.52
113	-43766	8.30	155	-43133	8.20
114	-44898	8.65	156	-46300	9.17
115	-43766	8.30	157	-46300	9.17
116	-43766	8.30	158	-45127	8.81
117	-43766	8.30	159	-46300	9.17
118	-44898	8.65	160	-45127	8.81
119	-43766	8.30	161	-45127	8.81
120	-44898	8.65	162	-46300	9.17
121	-43766	8.30	163	-45127	8.81
122	-44898	8.65	164	-45127	8.81
123	-44898	8.65	165	-45127	8.81
124	-44898	8.65	166	-45127	8.81
125	-43766	8.30	167	-46300	9.17
126	-46011	9.00	168	-44160	8.52

### Table S1 (continued)

PCB Congener	$\Delta H_{\rm S, XAD}$	log K <sub>XAD/A</sub> (20°C)	PCB Congener	$\Delta H_{\rm S, XAD}$	log K <sub>XAD/A</sub> (20°C)
IUPAC#	J/mol	(-)	IUPAC#	J/mol	(-)
169	-47436	9.53	190	-46488	9.32
170	-46488	9.32	191	-46488	9.32
171	-46488	9.32	192	-46488	9.32
172	-46488	9.32	193	-46488	9.32
173	-46488	9.32	194	-47850	9.83
174	-45503	9.03	195	-46846	9.54
175	-45503	9.03	196	-46846	9.54
176	-44435	8.70	197	-45737	9.20
177	-45503	9.03	198	-46846	9.54
178	-45503	9.03	201	-46846	9.54
179	-44435	8.70	199	-45737	9.20
180	-46488	9.32	200	-45737	9.20
181	-45503	9.03	202	-45737	9.20
182	-45503	9.03	203	-46846	9.54
183	-45503	9.03	204	-45737	9.20
184	-44435	8.70	205	-47850	9.83
185	-45503	9.03	206	-48189	10.05
186	-44435	8.70	207	-47039	9.70
187	-45503	9.03	208	-47039	9.70
188	-44435	8.70	209	-48341	10.20
189	-47702	9.69			

## Table S1 (continued)

PCB Congener	$\Delta H_{\rm S, PUF}$	log K <sub>PUF/A</sub> (20°C)	PCB Congener	$\Delta H_{\rm S, PUF}$	log K <sub>PUF/A</sub> (20°C)
IUPAC#	J/mol	(-)	IUPAC#	J/mol	(-)
1	-61893	4.81	43	-81562	6.86
2	-62965	5.01	44	-82306	6.98
3	-63184	5.05	45	-80818	6.74
4	-68160	5.43	46	-81463	6.84
5	-69326	5.65	47	-81941	6.92
6	-69231	5.63	48	-81829	6.90
7	-68784	5.56	49	-81764	6.89
8	-69450	5.67	50	-80337	6.66
9	-68608	5.53	51	-80922	6.75
10	-67945	5.40	52	-81584	6.86
11	-70302	5.83	53	-80745	6.73
12	-70535	5.87	54	-79903	6.59
13	-70522	5.86	55	-83696	7.23
14	-69821	5.75	56	-84233	7.32
15	-70745	5.90	57	-82634	7.06
16	-75592	6.26	58	-83150	7.14
17	-75050	6.18	59	-82212	6.96
18	-74874	6.15	60	-83919	7.26
19	-74031	6.01	61	-83567	7.21
20	-76663	6.46	62	-81945	6.92
21	-76358	6.41	63	-82857	7.09
22	-76887	6.50	64	-82461	7.00
23	-75296	6.24	65	-82203	6.96
24	-74904	6.15	66	-83691	7.23
25	-76122	6.37	67	-82900	7.10
26	-75941	6.34	68	-82608	7.05
27	-75424	6.24	69	-81377	6.83
28	-76345	6.41	70	-83597	7.21
29	-75563	6.28	71	-83024	7.10
30	-74487	6.08	72	-82427	7.02
31	-76165	6.38	73	-81941	6.92
32	-75721	6.28	74	-83120	7.13
33	-76801	6.48	75	-81597	6.86
34	-75717	6.31	76	-83661	7.22
35	-77872	6.68	77	-85442	7.54
36	-76845	6.52	78	-84728	7.42
37	-78092	6.72	79	-84354	7.36
38	-77365	6.60	80	-83387	7.20
39	-77008	6.54	81	-84922	7.45
40	-83029	7.10	82	-84190	7.13
41	-82624	7.03	83	-87428	7.65
42	-82487	7.01	84	-86684	7.53

**Table S2** PUF-air partition coefficients ( $K_{PUF/A}$ ) and sorption enthalpies ( $\Delta H_{S, PUF}$ , J/mol) for PCBs

PCB Congener	$\Delta H_{\rm S, PUF}$	log K <sub>PUF/A</sub> (20°C)	PCB Congener	$\Delta H_{\rm S, PUF}$	log K <sub>PUF/A</sub> (20°C)
IUPAC#	J/mol	(-)	IUPAC#	J/mol	(-)
85	-87948	7.73	127	-89622	8.05
86	-87578	7.67	128	-97089	8.63
87	-87772	7.71	129	-96577	8.55
88	-85226	7.29	130	-96027	8.46
89	-86929	7.57	131	-94230	8.17
90	-86886	7.56	132	-95283	8.34
91	-86142	7.44	133	-94965	8.28
92	-86710	7.53	134	-94307	8.18
93	-85308	7.31	135	-94221	8.16
94	-85867	7.40	136	-93477	8.04
95	-85966	7.41	137	-96036	8.46
96	-85123	7.28	138	-96294	8.50
97	-87695	7.69	139	-94337	8.18
98	-85820	7.39	140	-94333	8.18
99	-87166	7.61	141	-94372	8.19
100	-85278	7.30	142	-94836	8.26
101	-86985	7.58	143	-95017	8.29
102	-86134	7.44	144	-93507	8.05
103	-85097	7.27	145	-92664	7.91
104	-84302	7.14	146	-95240	8.33
105	-89755	8.05	147	-93757	8.09
106	-88615	7.87	148	-93357	8.02
107	-88637	7.87	149	-94488	8.21
108	-88701	7.88	150	-92613	7.90
109	-87720	7.70	151	-93585	8.06
110	-88245	7.78	152	-92746	7.92
111	-87553	7.70	153	-95498	8.37
112	-86731	7.54	154	-93623	8.07
113	-87161	7.61	155	-91749	7.76
114	-88869	7.91	156	-97782	8.77
115	-86873	7.56	157	-98096	8.82
116	-87544	7.67	158	-95786	8.42
117	-87677	7.69	159	-97111	8.63
118	-88903	7.91	160	-95511	8.37
119	-87381	7.64	161	-94703	8.24
120	-87816	7.74	162	-97090	8.65
121	-86306	7.47	163	-95868	8.43
122	-89497	8.01	164	-96642	8.56
123	-88955	7.92	165	-95090	8.30
124	-88779	7.89	166	-96530	8.54
125	-88288	7.79	167	-97300	8.69
126	-90650	8.22	168	-95778	8.42

## Table S2 (continued)

Table S2 (continued)

PCB Congener	$\Delta H_{\rm S, PUF}$	log K <sub>PUF/A</sub> (20°C)	PCB Congener	$\Delta H_{S, PUF}$	log K <sub>PUF/A</sub> (20°C)
IUPAC#	J/mol	(-)	IUPAC#	J/mol	(-)
169	-99189	9.02	190	-103081	9.23
170	-103610	9.31	191	-102617	9.15
171	-101262	8.93	192	-102006	9.05
172	-102548	9.14	193	-102698	9.16
173	-101524	8.97	194	-110083	9.99
174	-101813	9.02	195	-108578	9.74
175	-100196	8.76	196	-107779	9.62
176	-99366	8.62	197	-105431	9.23
177	-101426	8.96	198	-107490	9.57
178	-100303	8.78	201	-107856	9.63
179	-99448	8.64	199	-106747	9.45
180	-102913	9.20	200	-106643	9.43
181	-100978	8.89	202	-105590	9.26
182	-100948	8.88	203	-107671	9.60
183	-100475	8.80	204	-105598	9.26
184	-98588	8.50	205	-109911	9.96
185	-100802	8.86	206	-113507	10.39
186	-99959	8.72	207	-111159	10.00
187	-100544	8.82	208	-111236	10.02
188	-98669	8.51	209	-116882	10.77
189	-104617	9.50			

### Detailed information on the depuration compounds and spiking procedures

*PUF*. Before sampling and after cleaning, the three cylindrical PUF layers were fortified with three different groups of depuration compounds (DCs): 15 mL of 1.4 ng/mL PCB-36 and PCB-186 in hexane were applied to the outer layer, 15 mL of 1.4 ng/mL PCB-38 and PCB-188 in hexane were applied to the middle layer, and 15 mL of 1.4 ng/mL PCB-39 and PCB-190 in hexane were applied to the inner layer. Based on a pre-test, 15 mL of solvent was sufficient to fully wet the PUF sheets, allowing the DCs to achieve a relatively uniform distribution in the PUF. When applying the DCs, each PUF sheet was placed on a piece of aluminum foil (baked for >4 hr at 450 °C), the 15 mL DC solution was spiked evenly onto the PUF using a pipette. The spiked PUF sheets were placed in a fume hood for  $\sim$  1 h to let the solvent evaporate before assembling the sheets into the concentrically layered PUF cylinder.

*XAD*. 200 g, 250 g, and 450 g clean XAD-2 resin were transferred into three glass jars in order to be used to fill the inner, middle and outer layer of the mesh cylinders, respectively. To the jar containing 200 g XAD (to be used to fill the inner layer) 4000 ng <sup>13</sup>C-PCB-1 and 3500 ng PCB-36 in 10 ml hexane was added; to the jar containing 250 g XAD (to be used to fill the middle layer) 4000 ng <sup>13</sup>C-PCB-4 and 3500 ng PCB-38 in 10 ml hexane was added; to the jar containing 450 g XAD (to be used to fill the outer layer) 8000 ng <sup>13</sup>C-PCB-8 and 7000 ng PCB-39 in 10ml hexane was added. The spiked XAD was shaken in the jars to uniformly distribute the spiked DCs. Since not all the prepared XAD was used, the initial DC levels in each of the XAD layers was determined from the duplicated blanks we prepared assuming that the DCs are uniformly distributed in the XAD in the glass jars.



**Figure S1** Illustration of the sampling scheme in this study.



Figure S3 Reproducibility of the duplicated samples as represented by the relative difference of the sampling rate R (m<sup>3</sup>/h) between duplicates. The relative difference is defined as R - R.

$$\frac{R_1 - R_2}{0.5(R_1 + R_2)}$$



**Figure S4** Analytical procedure recovery of the surrogate standards spiked prior to sample extraction.

Table S3         Limit of detection <sup>a</sup> (LOD) of PCBs analyzed using HRGC/MS									
PCB Homolog	g Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-		
LOD (pg/sampl	<b>e)</b> 10	20	5	5	5	5	7		

<sup>a</sup> defined as the chemical amount corresponding to the signal-to-noise ratio of 3 LOD of each PCB homolog is average of the LOD of each congener in the homolog group.

# Description of the two-layer mass balance model used to derive effective diffusivities of PCBs through the passive sampling medium

The mass balance of the chemical in the outer (Layer 1) and inner layer (Layer 2) can be expressed as:

$$\frac{dm_{1}}{dt} = k_{A}A_{1}(C_{A} - C_{1} / K_{SA}) - \frac{D_{E}}{\delta}A_{2}(C_{1} - C_{2}) \quad \text{(Eq. S6)}$$
$$\frac{dm_{2}}{dt} = \frac{D_{E}}{\delta}A_{2}(C_{1} - C_{2}) \quad \text{(Eq. S7)}$$

where  $m_1$  and  $m_2$  [dimension: M] are the amounts of the chemical sequestered in Layer 1 and 2; t [T] is time;  $k_A$ [LT<sup>-1</sup>] is the mass transfer coefficient for chemical crossing the air-side boundary layer;  $A_I$  [L<sup>2</sup>] is the surface area between air and Layer 1;  $C_A$  [ML<sup>-3</sup>] is the chemical concentration in air;  $C_1$  and  $C_2$  [ML<sup>-3</sup>] are the concentrations of the chemical sequestered in Layer 1 and 2;  $K_{SA}$  [dimensionless] is the partition coefficient between the passive sampling medium (PSM) and air;  $D_E$  [L<sup>2</sup>T<sup>-1</sup>] is the effective diffusion coefficient of the chemical in the PSM;  $\delta$  [L] is the diffusion length of the chemical within the PSM.



Figure S5 Illustration of the two-layer mass balance model used to derive effective diffusivities of PCBs through the passive sampling medium.

The measured data indicate that the amount of chemical penetrating to Layer 2 is less than 1% of that staying in Layer 1, i.e. the chemical exchange between outer and inner layer is negligible compared to the chemical transfer from air to Layer 1. Thus, Eq. S6 and Eq. S7 can be simplified to:

$$\frac{dm_1}{dt} \Box k_A A_1 (C_A - C_1 / K_{SA}) \quad \text{(Eq. S8)}$$
$$\frac{dm_2}{dt} \Box \frac{D_E}{\delta} A_2 C_1 \quad \text{(Eq. S9)}$$

Further, the uptake kinetics of the chemical in the first layer was generally linear, thus Eq. S8 can be further simplified to:

$$\frac{dm_1}{dt} \Box k_A A_1 C_A \text{ (Eq. S10)}$$

Integrated from 0 to t, Eq. S10 becomes:

$$V_1C_1(t) = m_1(t) = k_A A_1 C_A t + m_1(0)$$
 (Eq. S11)

From Eq. S9 and Eq. S11,

$$\frac{dm_2}{dt} = \frac{D_E}{\delta} \frac{A_2}{V_1} [k_A A_1 C_A t + m_1(0)]$$
 (Eq. S12)

Integrated from 0 to t, Eq. S12 becomes:

$$m_2(t) = \frac{1}{2} \frac{D_E}{\delta} \frac{A_2}{V_1} k_A A_1 C_A t^2 + \frac{D_E}{\delta} \frac{A_2}{V_1} m_1(0) t + m_2(0) \quad \text{(Eq. S13)}$$

Because  $k_A$  depends on the boundary layer thickness, which varies by the air conditions around the PSM and is highly uncertain, the term  $k_A A_1 C_A t$  in Eq. S13 can be replaced with that in Eq. S11:

$$m_2(t) = \frac{1}{2} \frac{D_E}{\delta} \frac{A_2}{V_1} [m_1(0) + m_1(t)]t + m_2(0)$$
 (Eq. S14)

In the experiment, different PCB congeners sequestered in Layer 1 and 2  $(m_1, m_2)$  were measured at seven time points. Let  $X_t = [m_1(0) + m_1(t)]t$  and  $Y_t = m_2(t)$ .  $X_t$  and  $Y_t$  can be plotted against each other and subjected to linear least squares fitting. The slope of the fitted line is equal to  $D_E A_2 / (2\delta V_1)$ . From the slope, the mass transfer coefficient from Layer 1 to Layer 2 (defined as  $k_{PSM12} = D_E/\delta$ ) can be calculated, because the dimensional parameters  $A_2$  and  $V_1$  are known. Furthermore, if the diffusion length within the PSM is known, the effective diffusion coefficient in the PSM ( $D_E$ ) can be derived.

		PUF		XAD	XAD		
PCB Homolog	IUPAC #	Sampling Rate (m <sup>3</sup> /d)	R <sup>2</sup>	Sampling Rate (m <sup>3</sup> /d)	R <sup>2</sup>		
Mono-	#1	0.16	0.98	0.23	0.96		
Mono-	#3	0.19	0.99	0.27	0.98		
Mono-	#2	0.13	0.97	0.20	0.98		
Di-	#10	0.10	0.95	0.17	0.95		
Di-	#4	0.11	0.96	0.19	0.97		
Di-	#9	0.08	0.96	0.12	0.91		
Di-	#7	0.14	0.96	0.18	0.97		
Di-	#6	0.14	0.98	0.19	0.98		
Di-	#8#5	0.14	0.97	0.18	0.98		
Di-	#11	0.12	0.96	0.17	0.97		
Di-	#13#12	0.12	0.97	0.17	0.91		
Di-	#15	0.14	0.96	0.20	0.97		
Tri-	#19	0.14	0.99	0.21	0.99		
Tri-	#18	0.15	0.98	0.20	0.99		
Tri-	#17	0.15	0.99	0.20	0.99		
Tri-	#24	0.14	0.97	0.21	0.98		
Tri-	#27	0.15	0.99	0.20	0.99		
Tri-	#32	0.15	0.99	0.21	0.98		
Tri-	#16	0.15	0.99	0.22	0.98		
Tri-	#34	0.11	0.88	0.20	0.88		
Tri-	#29	0.15	0.90	0.23	0.97		
Tri-	#26	0.15	0.99	0.20	0.98		
Tri-	#25	0.15	0.98	0.21	0.98		
Tri-	#31	0.14	0.99	0.20	0.98		
Tri-	#28	0.15	0.99	0.20	0.99		
Tri-	#22	0.15	0.99	0.19	0.98		
Tri-	#35	0.17	0.97	0.26	0.78		
Tri-	#37	0.15	0.99	0.19	0.98		

Table S4 Congener-specific passive air sampling rates of PCBs derived using linear least squares fitting

DCB Homolog	DCB Congener	PUF	PUF		XAD		
PCB Holliolog	IUPAC #	Sampling Rate (m <sup>3</sup> /d)	R <sup>2</sup>	Sampling Rate (m <sup>3</sup> /d)	R <sup>2</sup>		
Tetra-	#53	0.15	0.99	0.18	0.98		
Tetra-	#51	0.15	0.99	0.20	0.98		
Tetra-	#45	0.16	0.99	0.18	0.98		
Tetra-	#46	0.15	0.99	0.18	0.98		
Tetra-	#52#69	0.16	0.99	0.22	0.98		
Tetra-	#43#49	0.15	0.99	0.18	0.99		
Tetra-	#48#47	0.16	0.99	0.18	0.98		
Tetra-	#44	0.15	0.99	0.14	0.97		
Tetra-	#42	0.16	0.98	0.19	0.99		
Tetra-	#64	0.16	0.98	0.18	0.99		
Tetra-	#71	0.15	0.99	0.18	0.98		
Tetra-	#40	0.15	0.99	0.18	0.98		
Tetra-	#67	0.15	0.94	0.17	0.97		
Tetra-	#63	0.16	0.98	0.18	0.98		
Tetra-	#74	0.16	0.99	0.18	0.98		
Tetra-	#70	0.15	0.98	0.17	0.97		
Tetra-	#66	0.16	0.98	0.18	0.98		
Tetra-	#55	0.06	0.99	0.22	0.82		
Tetra-	#60	0.15	0.96	0.17	0.99		
Tetra-	#56	0.15	0.98	0.18	0.98		
Tetra-	#78	0.16	0.96	0.14	0.99		
Tetra-	#81	0.15	0.95	0.15	0.94		
Tetra-	#77	0.11	0.90	0.15	0.92		
Tetra-	#96	0.08	0.98	0.20	0.94		
Tetra-	#103	0.08	0.97	0.20	0.96		
Penta-	#100	0.12	0.98	0.20	0.96		
Penta-	#94	0.14	0.98	0.24	0.97		
Penta-	#102#93	0.17	0.99	0.15	0.96		
Penta-	#98#95	0.08	0.96	0.20	0.98		
Penta-	#91	0.11	0.99	0.18	0.97		
Penta-	#92	0.12	0.99	0.19	0.98		
Penta-	#84	0.09	0.99	0.17	0.97		
Penta-	#89	0.08	0.95	0.17	0.89		
Penta-	#90#101	0.07	0.96	0.19	0.98		
Penta-	#99	0.11	0.99	0.17	0.97		
Penta-	#112#119	0.11	0.99	0.17	0.97		
Penta-	#83	0.10	0.98	0.18	0.97		
Penta-	#86#117#97	0.11	0.98	0.18	0.97		
Penta-	#85	0.09	0.98	0.16	0.97		
Penta-	#87#115	0.10	0.98	0.17	0.93		
Penta-	#120#110	0.07	0.97	0.16	0.86		
Penta-	#82	0.08	0.96	0.16	0.96		
Penta-	#124	0.09	0.98	0.16	0.97		
Penta-	#109#107	0.10	0.98	0.16	0.97		
Penta-	#118	0.09	0.98	0.15	0.97		
Penta-	#114	0.10	0.94	0.15	0.93		
Penta-	#122	0.10	0.87	0.19	0.96		

### Table S4 (continued)

		PUF		XAD	XAD		
PCB Homolog	IUPAC #	Sampling Rate (m <sup>3</sup> /d)	R <sup>2</sup>	Sampling Rate (m <sup>3</sup> /d)	R <sup>2</sup>		
Hexa-	#150	0.11	0.92	0.18	0.96		
Hexa-	#152	0.10	0.94	0.17	0.97		
Hexa-	#145	0.09	0.85	0.17	0.97		
Hexa-	#136	0.08	0.98	0.14	0.98		
Hexa-	#154	0.10	0.97	0.16	0.98		
Hexa-	#151	0.10	0.98	0.14	0.99		
Hexa-	#135	0.10	0.98	0.14	0.99		
Hexa-	#144	0.10	0.98	0.13	0.99		
Hexa-	#147	0.09	0.97	0.15	0.98		
Hexa-	#149#139	0.10	0.98	0.14	0.99		
Hexa-	#143	0.10	0.83	0.14	0.94		
Hexa-	#134	0.10	0.98	0.14	0.99		
Hexa-	#131	0.09	0.97	0.14	0.99		
Hexa-	#146	0.09	0.98	0.14	0.98		
Hexa-	#132	0.08	0.97	0.13	0.98		
Hexa-	#153	0.08	0.98	0.12	0.98		
Hexa-	#141	0.07	0.98	0.13	0.98		
Hexa-	#137	0.09	0.98	0.13	0.99		
Hexa-	#130	0.08	0.98	0.12	0.99		
Hexa-	#164#163	0.09	0.97	0.13	0.99		
Hexa-	#138	0.08	0.85	0.12	0.99		
Hexa-	#158	0.09	0.98	0.12	0.99		
Hexa-	#129	0.09	0.97	0.12	0.99		
Hexa-	#166	0.10	0.87	0.13	0.98		
Hexa-	#128	0.08	0.95	0.13	0.98		
Hexa-	#167	0.12	0.95	0.15	0.99		
Hexa-	#156	0.13	0.91	0.15	0.99		
Hepta-	#179	0.09	0.98	0.13	0.98		
Hepta-	#176	0.09	0.98	0.13	0.98		
Hepta-	#178	0.08	0.89	0.13	0.98		
Hepta-	#175	0.09	0.89	0.10	0.96		
Hepta-	#182#187	0.08	0.96	0.12	0.98		
Hepta-	#183	0.08	0.94	0.12	0.98		
Hepta-	#185	0.08	0.96	0.12	0.98		
Hepta-	#174	0.08	0.94	0.12	0.98		
Hepta-	#177	0.08	0.93	0.12	0.97		
Hepta-	#171	0.08	0.93	0.12	0.94		
Hepta-	#172	0.09	0.81	0.11	0.99		
Hepta-	#180	0.12	0.85	0.11	0.98		
Hepta-	#170	0.12	0.83	0.10	0.97		

## Table S4 (continued)

Table	<b>Table S5</b> Passive air sampling rates determined in different studies using XAD and PUF as							
	PSM.							
PSM	R (m³/d)	SA <sup>a</sup> (dm <sup>2</sup> )	SR <sup>b</sup> (m³/d/dm²)	Environment Type	Chemical	Study <sup>c</sup>		
	0.1-0.3	0.94	0.11-0.32	indoor	PCBs	this study		
	0.4-2.3	0.63	0.63-3.7	outdoor	pesticides	Hayward, et al. (2010)		
XAD	0.8-5.4	1.26	0.63-4.3	outdoor	pesticides	Gouin, et al. (2008)		
	0.4-2.2	1.26	0.32-1.7	outdoor	pesticides	Wania, et al. (2003)		
	0.06-0.2	3.02	0.02-0.07	indoor	PCBs	this study		
	0.57-1.55	3.6	0.16-0.43	indoor	PCBs	Hazrati and Harrad (2007)		
	2.0-8.3	3.65	0.55-2.27	indoor	PCBs	Shoeib and Harner (2002)		
PUF	0.66-24	3.6	0.18-6.7	outdoor	PCBs	Melymuk, et al. (2010)		
	2.9-7.3	3.6	0.81-2.03	outdoor	PCBs	Chaemfa, et al. (2008)		
	$0.10 \pm 0.01$	1.88	0.053 ± 0.005	indoor	PAHs	Tao, et al. (2007)		
	$0.38 \pm 0.51$	2.42	$0.16 \pm 0.21$	outdoor	PAHs	Tao, et al. (2009)		
<sup>a</sup> surfa	ce area betwe	en PSM a	nd air; <sup>b</sup> surface a	rea normalized s	ampling rate;	<sup>c</sup> reference 5-12		



**Figure S6** Relationship between homolog-specific molecular diffusivities in air and passive air sampling rates. The molecular diffusivities in air are derived from the Fuller-Schettler-Giddings equation<sup>13</sup>; the passive air sampling rate is based on the median of the congener-specific sampling rates in each homolog group.

#### Transfer kinetics of the depuration compounds

The depuration compounds spiked to the inner PUF layer (PCB-39 and PCB-190) gradually migrated outward during deployment (Figure S6). PCB-39 and PCB-190 decreased in the inner layer and increased in the middle and outer layer. The amount accumulated in the outer layer was lower than that in the middle layer. The mass balance of the DCs was checked by the sum of the DCs in the three layers. The sum of PCB-39 and PCB-190 ranged from 80 % to 100 % of the initially spiked amount. After 84 d,  $\sim$ 20 % and  $\sim$ 10 % of the initially spiked PCB-39 of PCB-190 had move into the middle and inner layers.

The depuration compounds spiked to the middle PUF layer (PCB-38 and PCB-188) migrated both to the inner and outer layer during deployment (Figure S6). No difference was observed between the amount in the inner and outer layer. The sum of PCB-38 and PCB-188 in the three layers ranged from 90 % to 110 % of the initially spiked amount. After 84 d,  $\sim$ 30 % and  $\sim$ 20 % of the initially spiked PCB-38 of PCB-180 had moved into the inner and outer layers.

The depuration compounds spiked to the outer PUF layer (PCB-36 and PCB-186) migrated inward to the middle and inner layer during deployment (Figure S6). Similar to the DCs spiked to the inner layer, higher amounts were detected in the adjacent layer. The sum of PCB-186 in the three layers ranged from 60 % to 100 % of the initially spiked amount. For PCB-36, the sum of the three layers ranged from 60 % to 140 % of the initially spiked amount; the amount in the outer layer appeared to increase gradually. Although PCB-36 is a non-Aroclor PCB<sup>14</sup> and had not been reported in PCB air profiles, from our low volume sampler analysis, we found PCB-36 had a level of ~0.7 ng/m<sup>3</sup> in the indoor air we sampled. This explains the increasing levels of PCB-36 in the outer layer of both PUF and XAD. Up to now, except for some studies on PCB-11,<sup>15,16</sup> few non-Aroclor PCBs have been analyzed and reported. Considering the likelihood of occurrence and toxicity of these congeners, further studies on these non-Aroclor PCBs are warranted.

PCBs sorb more strongly to XAD than to PUF.<sup>1</sup> Therefore, more volatile PCB congeners (mono-/diand tri-CBs) were spiked onto XAD to increase the likelihood of observing a transfer between the XAD layers. Nevertheless, even for the most volatile congeners (<sup>13</sup>C PCB-1) spiked to the inner XAD layer, no significant transfer to the other layers was observed. This is also the same for all the other di- and tri-CBs spiked as DCs to the inner and middle XAD layer (Figure S7).

Overall, the results for the DCs serve as further evidence of the existence of kinetic resistance to chemical transfer within the PSM. They also provide further evidence of a relationship between a chemical's mobility within a PSM and the  $K_{PSM/A}$ . We can also conclude that DCs initially present in the inner part of PSM are less likely to evaporate to the ambient air than those closer to the surface.



Figure S7 Changes of the amounts of depuration compounds (tri- and hepta-CBs) spiked to the inner, middle, and outer layer of PUF. The amount of chemicals present in each layer  $(M_i)$  was normalized to the amount  $(M_0)$  in the field blanks (samples retrieved at t=0).



**Figure S8** Changes of the amounts of depuration compounds (mono-/di- and tri-CBs) spiked to the inner, middle, and outer layer of XAD. The amount of chemicals present in each layer  $(M_i)$  was normalized to the amount  $(M_0)$  in the field blanks (samples retrieved at t=0).



**Figure S9** Illustration of the sensitivity of  $D_{\text{EPUF}}$  to the variations of  $D_{\text{A}}$  and  $K_{\text{PUF/A}}$ . (a) based on  $f/r_{\text{SA}}$  value of 0.18; (B) based on  $f/r_{\text{SA}}$  value of 0.45.

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