

Adsorption versus Absorption of Polychlorinated Biphenyls onto Solid-Phase Microextraction Coatings

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Absorption-based polymeric solid-phase microextraction (SPME) fibers with poly(dimethylsiloxane) (PDMS) coatings were used to determine the partitioning coefficients of polychlorinated biphenyls (PCBs) between the sorptive fiber coatings and water. Previous models showing very good correlations between octanol–water partitioning coefficients (K_{ow}) and absorption-based fiber–water partitioning coefficients (K_{dv}) for low-molecular-weight analytes failed to predict K_{dv} values for PCBs. In fact, K_{dv} values for PCBs were 1–7 orders of magnitude lower than those predicted by K_{ow} and actually showed a strong negative correlation between K_{ow} and K_{dv} for higher molecular weight analytes (MW > ~200). K_{dv} values obtained using PDMS fibers with 7- and 100- μ m coatings also disagree, demonstrating that K_{dv} cannot be used to describe the partitioning behavior of PCBs between PDMS and water. However, when PCB partitioning coefficients were calculated on the basis of surface area (K_{ds}), the K_{ds} values obtained using 7- and 100- μ m PDMS fibers agreed reasonably well, demonstrating that surface adsorption is the primary mechanism controlling PCB (and likely other higher molecular weight solutes) partitioning from water to SPME sorbents.

A number of investigators have reported the correlation between octanol–water partitioning coefficients (K_{ow}) and solid-phase microextraction (SPME) coating–water partitioning coefficients (K_{dv}).^{1–5} This correlation was used to predict SPME fiber–water partitioning behavior. These correlations have mostly been applied for analytes having low molecular weights, such as benzene (MW = 78), toluene (MW = 92), and xylenes (MW =

106).¹ However, the correlation between K_{ow} and K_{dv} appears to fail as the molecular weights of the analytes increase, and the poor correlations for analytes such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) have generally been ignored.^{4,6,7} These results suggest that higher molecular weight analytes may be adsorbed onto the surface of the polymeric fibers rather than absorbed into the polymeric phase of the SPME fibers. To investigate the relative importance of these two mechanisms, we determined PCB partitioning coefficients between poly(dimethylsiloxane) (PDMS) (both 7- and 100- μ m coatings) and water. Partitioning coefficients were calculated on the basis of sorbent volume (K_{dv}) and surface area (K_{ds}).

EXPERIMENTAL SECTION

A mixture of 21 PCBs ranging from di- to decachlorobiphenyls (100 μ g/mL each, AccuStandard Inc., New Haven, CT) was diluted 1:10 000 in acetone to prepare the spiking standard. HPLC-grade water (Fisher Scientific, Pittsburgh, PA) was spiked with 10 μ L of the standard solution to achieve a concentration of 50 ppt for each individual congener. This concentration was chosen because it is well within the linear calibration range for all of the PCB congeners⁷ and because it is at least an order of magnitude below the solubility limit for the least soluble congeners.⁸

Commercially available 7- and 100- μ m film thickness PDMS fibers (Supelco, Bellefonte, PA) were used in this study. Based on the coating dimensions reported by the manufacturer, the volumes of the PDMS phases were 0.026 and 0.612 μ L, respectively, while the surface areas of the PDMS fibers were 3.90 and 9.42 mm² for 7- and 100- μ m fibers, respectively. New fibers were used to eliminate the eventual carryover resulting from old fibers.⁷ All of the fibers were cleaned for 10 min at 300 °C before each SPME extraction.

The PCB-spiked water was loaded into a 2-mL silanized vial^{4,6,7} with a Teflon-lined septum cap, and a magnetic stir bar (8-mm

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Table 1. Comparison of Volume-Based PDMS/Water Partitioning Coefficients (K_{dv}) for PCBs Obtained Using 7- and 100- μm Fibers

	MW ^a	K_{ow} ^{8,9}	K_{dv}			5 h K_{dv} ratio, 7 μm /100 μm
			100 μm		7 μm , 5 h ^b	
			5 h ^b	24 h ^b		
PCB-8	223	210 000	11 800 \pm 1 100	12 400 \pm 2 300	32 300 \pm 4 800	3
PCB-18	258	440 000	10 500 \pm 1 200	10 800 \pm 1 900	32 400 \pm 4 400	3
PCB-28	258	550 000	8 700 \pm 870	7 650 \pm 910	35 100 \pm 6 900	4
PCB-44	292	4 700 000	7 670 \pm 1 100	6 290 \pm 1 400	55 600 \pm 10 000	7
PCB-52	292	1 800 000	7 270 \pm 620	7 420 \pm 1 900	46 700 \pm 9 600	6
PCB-66	292	4 700 000	8 530 \pm 920	7 500 \pm 1 600	70 300 \pm 13 900	8
PCB-77	292	3 300 000	8 320 \pm 700	6 740 \pm 1 500	83 600 \pm 12 500	10
PCB-101	326	7 100 000	3 750 \pm 630	3 670 \pm 840	35 900 \pm 7 100	10
PCB-105	326		3 130 \pm 640	2630 \pm 630	36 700 \pm 3 200	12
PCB-118	326	2 500 000	3 310 \pm 660	3 640 \pm 1 100	36 700 \pm 4 900	11
PCB-126	326		1840 \pm 300	1670 \pm 390	33 200 \pm 5 000	18
PCB-128	361	28 000 000	932 \pm 210	755 \pm 120	18 300 \pm 1 500	20
PCB-138	361	10 000 000	2 280 \pm 530	2 350 \pm 350	31 100 \pm 2 600	14
PCB-153	361	28 000 000	2 500 \pm 790	2 620 \pm 660	37 500 \pm 5 100	15
PCB-170	395		823 \pm 280	922 \pm 250	17 100 \pm 3 300	21
PCB-180	395		868 \pm 140	825 \pm 270	16 300 \pm 2 900	19
PCB-187	395		1 540 \pm 470	1 830 \pm 330	24 000 \pm 1 500	16
PCB-195	430		510 \pm 140	563 \pm 29	9 930 \pm 500	19
PCB-201	430		967 \pm 220	1 190 \pm 24	17 000 \pm 1 200	18
PCB-206	464	1 400 000 000	299 \pm 60	279 \pm 19	6 230 \pm 760	21
PCB-209	499	9 100 000 000	252 \pm 58	272 \pm 52	5 650 \pm 1100	22

^a Average molecular weight. ^b SPME/water equilibration time.

length \times 1.5-mm diameter, Fisher Scientific) was placed inside the loaded sample vial for agitation. *Please note that new stir bars were used for each sample to eliminate the stir bar contamination that was encountered in our previous study.*⁷ The fiber was withdrawn inside the needle of the holder, and then the vial septum was pierced with the needle. Once the needle had penetrated the septum of the vial, the plunger on the fiber holder was depressed to expose the fiber to the water sample for 5 or 24 h. The water sample was continuously agitated with the stir bar on a stir plate revolving at \sim 1000 rpm during the 5- or 24-h extractions. Once the extraction was completed, the fiber was withdrawn back inside the fiber holder, removed from the water sample, and analyzed immediately.

The extracted PCBs in the fiber were analyzed using an electronic pressure-controlled Hewlett-Packard 5890 Series II gas chromatograph (GC) equipped with a ⁶³Ni electron capture detector (ECD) and a split/splitless injection port. The column was a 25-m HP-5 with an internal diameter of 0.32 mm and a stationary phase thickness of 0.17 μm (Hewlett-Packard, Little Falls, PA). Immediately after the SPME extraction, the SPME fiber was inserted into the 300 $^{\circ}\text{C}$ GC injection port and desorbed for 1 min in the splitless mode. The desorbed PCBs were focused at the column inlet by maintaining the oven at 60 $^{\circ}\text{C}$ during the desorption. Once the desorption was completed, the split vent was opened, and the GC run was started in the normal manner. The initial temperature (60 $^{\circ}\text{C}$) was ramped at 25 $^{\circ}\text{C}/\text{min}$ to 130 $^{\circ}\text{C}$, then at 8 $^{\circ}\text{C}/\text{min}$ to 320 $^{\circ}\text{C}$, and held at 320 $^{\circ}\text{C}$ for 5 min. The detector temperature was maintained at 300 $^{\circ}\text{C}$. The GC/ECD response was calibrated by solvent injections of the PCB standard into a cool on-column injector prior to SPME analyses.

Definition of the Terms and Symbols Used in This Study.

Absorption. Analytes are absorbed into the polymeric phase on the SPME fibers, and the partitioning is described by the

conventional volume-based distribution coefficient:

$$K_{dv} = (M_f/V_f)/(M_w/V_w) \quad (1)$$

where M_f is the mass of analyte absorbed by the fiber, V_f is the volume of the fiber coating (0.026 and 0.612 μL for the 7- and 100- μm fibers, respectively), M_w is the mass of analyte remaining in the water after equilibration, and V_w is the volume of water.

Adsorption. Analytes are accumulated on the surface of the SPME fibers. A surface-based sorption partitioning coefficient is defined as

$$K_{ds} = (M_f/S_f)/(M_w/V_w) \quad (2)$$

where M_f is the mass of analyte adsorbed by the fiber, S_f is the surface area of the fiber coating (3.90 and 9.42 mm^2 for the 7- and 100- μm fibers, respectively), M_w is the mass of analyte remaining in the water after equilibration, and V_w is the volume of water. While K_{dv} is unitless, K_{ds} has units of centimeters (when the surface area of the fiber is expressed in square centimeters and the water volume is in cubic centimeters).

RESULTS AND DISCUSSION

PDMS fibers with coating thicknesses of 7 and 100 μm were used to determine the volume-based distribution coefficient K_{dv} of PCBs between PDMS and water. Since the 100- μm fiber may require a longer time to reach equilibrium than the 7- μm fiber, the SPME extraction using the 100- μm fiber was performed for 5 and 24 h to ensure equilibration. As shown in Table 1, the K_{dv} values obtained from 5- and 24-h SPME extractions agree very well, demonstrating that equilibration was reached within 5 h.

Table 2. Comparison of Volume-Based PDMS/Water Partitioning Coefficients (K_{dv}) Obtained Using 7-, 15-, and 100- μm PDMS Fibers, Reported in Refs 4 and 6

	MW	K_{ow}^4	K_{dv}		
			100 μm^6	7 μm^6	15 μm^4
naphthalene	128	1 020	705	514	1 020
anthracene	178	34 700	1 380	9 380	12 600
benz[a]anthracene	228	407 000	6 710	28 900	91 200
benzo[a]pyrene	252	2 750 000	2 980	18 400	72 400
PCB-18	258	437 000			87 100
PCB-87	326	7 080 000			77 600

Therefore, 5-h SPME sampling times were used for determining the partitioning coefficients for the remainder of the study.

Unlike previous reports of good agreement between K_{ow} and K_{dv} for low-molecular-weight analytes (such as benzene, toluene, and xylenes),¹ K_{dv} does not agree with K_{ow} for PCBs. As shown in Table 1, the K_{dv} values decrease with increasing molecular weight of the PCBs, while K_{ow} increases dramatically with PCB molecular weight. The K_{dv} values range from 1 to 2 orders of magnitude lower than the K_{ow} values for the low-molecular-weight PCB congeners to 7 orders of magnitude lower for the high-molecular-weight PCBs.

Negative correlations between K_{ow} and K_{dv} for analytes with higher molecular weights are also found in the literature, even though this phenomenon was generally ignored in those reports.^{4,6} For example, naphthalene's (MW = 128) K_{ow} of 1020 is nearly identical to the values of 705, 514, and 1020 (for 100-, 7-, and 15- μm fibers, respectively). However, the agreement becomes much worse with higher molecular weight PAHs. For example, K_{ow} and K_{dv} for benzo[a]pyrene (MW = 252) vary as much as 1000-fold, as shown in Table 2.⁶ Although only two PCB congeners (PCB-18 and PCB-87) have been reported,⁴ the K_{dv} values determined by a 15- μm PDMS fiber are 5–100 times lower than the K_{ow} values for the same congener (Table 2), again with the higher molecular weight compound showing the poorest agreement. Based on the K_{ow} and K_{dv} data reported in this study and in the literature, we can clearly conclude that K_{ow} cannot be used to anticipate the K_{dv} trend in SPME for PCBs and PAHs with molecular weights higher than that of naphthalene.

Comparison of the K_{dv} values for PCBs obtained using 7- and 100- μm fibers is also shown in Table 1. Based on the definition of K_{dv} , values should not change for the same analyte and the same fiber coating material, regardless of the coating thickness. However, Table 1 shows that the K_{dv} values of PCBs in a PDMS–water system obtained using a 7- μm fiber are 3–22 times higher than those obtained using the 100- μm fiber. The disagreement in K_{dv} values obtained using the same PDMS fibers was also reported in the literature for high-molecular-weight PAHs.⁶ As shown in Table 2, the K_{dv} values obtained using 7- and 15- μm fibers are 4–24 times higher than those obtained using the 100- μm fiber for higher molecular weight PAHs (e.g., anthracene, MW = 178; benz[a]anthracene, MW = 228; and benzo[a]pyrene, MW = 252), although the K_{dv} values obtained using all three fibers agree reasonably well for naphthalene (MW = 128). The disagreement in K_{dv} values for PDMS fibers with different coating thicknesses clearly demonstrates that K_{dv} is not valid to describe the sorption behavior of analytes having higher molecular weights.

Table 3. Comparison of Surface-Based Fiber/Water Partitioning Coefficients (K_{ds}) for PCBs Obtained Using PDMS-Coated Fibers

PCBs	MW	K_{ds}^a PDMS		K_{ds} ratios, ^b 7- μm PDMS/ 100- μm PDMS
		100 μm	7 μm	
PCB-8	223	76 \pm 7	22 \pm 3	0.28
PCB-18	258	68 \pm 7	22 \pm 3	0.32
PCB-28	258	57 \pm 5	23 \pm 4	0.42
PCB-44	292	50 \pm 7	37 \pm 6	0.75
PCB-52	292	47 \pm 4	31 \pm 6	0.66
PCB-66	292	55 \pm 6	47 \pm 9	0.85
PCB-77	292	54 \pm 5	56 \pm 8	1.03
PCB-101	326	24 \pm 4	24 \pm 4	0.99
PCB-105	326	20 \pm 4	25 \pm 2	1.2
PCB-118	326	22 \pm 4	25 \pm 3	1.1
PCB-126	326	12 \pm 2	22 \pm 3	1.8
PCB-128	361	6.1 \pm 1	12 \pm 1	2.0
PCB-138	361	15 \pm 3	21 \pm 2	1.4
PCB-153	361	16 \pm 5	25 \pm 3	1.5
PCB-170	395	5.3 \pm 2	11 \pm 2	2.1
PCB-180	395	5.6 \pm 1	11 \pm 2	1.9
PCB-187	395	10 \pm 3	16 \pm 1	1.6
PCB-195	430	3.3 \pm 0.9	6.6 \pm 0.3	1.9
PCB-201	430	6.3 \pm 1	11 \pm 1	1.8
PCB-206	464	1.9 \pm 0.4	4.2 \pm 0.5	2.1
PCB-209	499	1.6 \pm 0.4	3.8 \pm 0.8	2.3

^a The surface areas are 3.90 and 9.42 mm² for 7- and 100- μm PDMS fibers, respectively. K_{ds} is defined in eq 2, where the surface area of the fiber is expressed in cm² and the water volume is in cm³. ^b K_{ds} ratio is the K_{ds} value determined for the 7- μm fiber divided by the K_{ds} value determined for the 100- μm PDMS fiber.

Table 4. Comparison of Surface-Based PDMS/Water Partitioning Coefficients (K_{ds}) for PAHs Obtained Using 7- and 100- μm PDMS Fibers

	MW	K_{ds}^a	
		100 μm	7 μm
naphthalene	128	4.5	0.35
anthracene	178	8.9	6.4
benz[a]anthracene	228	43	20
benzo[a]pyrene	252	19	13

^a K_{ds} values were calculated using the K_{dv} values in Table 2 from ref 6 and the surface areas of the fibers.

Since the difference between the K_{dv} values for the two PDMS fibers increases with increasing molecular weight of the PCBs, the sorption mechanism of PCBs in a PDMS–water system may be controlled more by sorbent surface area than by sorbent volume. Therefore, we calculated the surface partitioning coefficient, K_{ds} , based on the fiber surface area (eq 2). As shown in Table 3, except for the lowest molecular weight PCBs, the K_{ds} values obtained using the 7- and 100- μm PDMS fibers agree much better than the K_{dv} values (Table 1). We also calculated the K_{ds} values on the basis of the K_{dv} values of PAHs obtained using 7- and 100- μm PDMS fibers and their surface areas.⁶ As shown in Table 4, the K_{ds} values of the 7- and 100- μm fibers agree well for the higher molecular weight PAHs, while the K_{dv} values determined using the 7- and 100- μm fibers do not agree well (Table 2). The better agreement in K_{ds} than in K_{dv} values between the 7- and 100- μm PDMS fibers clearly demonstrates that K_{ds} is more valid than K_{dv} for describing the sorption mechanisms of PCBs and PAHs in the SPME process. Thus, the dominant sorption

process for PCBs and PAHs on PDMS coatings is adsorption, especially for the higher molecular weight species.

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