# Determination of polydimethylsiloxane (PDMS)-seawater distribution coefficients for polychlorinated biphenyls and chlorinated pesticides by solid-phase microextraction

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**ABSTRACT -** Despite the growing popularity of solid-phase microextraction (SPME) among the community of analytical chemists, applications of SPME in the measurement of very hydrophobic organic compounds (VHOCs) have remained limited. This is due, in part, to the difficulty of calibrating SPME devices for VHOCs. Here, we present an analytical procedure used to determine the distribution coefficients ($K_f$ values) for a large suite of polychlorinated biphenyl (PCB) congeners and chlorinated pesticides between a polydimethylsiloxane (PDMS) phase (100 μm thickness) and seawater. Losses of analytes to sample containers and stirring bars were accounted for in the determination of $K_f$. The correlation between log $K_f$ and log $K_{ow}$, the octanol-water partition coefficient, was positively linear for PCB congeners with log $K_{ow}$ up to ~6.5, but became negatively linear for PCB congeners with log $K_{ow}$ >6.5. When grouped based on the number of chlorines (homolog), log $K_f$ increased linearly with increasing log $K_{ow}$ for homologs 3-5 and decreased for homologs 6-10. These findings were inconsistent with existing data acquired using thinner PDMS coatings (7 and 15 μm), which exhibited a positively linear relationship between log $K_f$ and log $K_{ow}$ for all PCB congeners. We postulate that the larger PCB congeners cannot readily sorb into the bulk PDMS phase, as would be required to maintain a consistent sorptive capacity for the thick 100 μm fiber coating. This effectively lowers the sorption capacity of PDMS-coated SPME devices for high molecular weight PCB congeners. This hypothesis contributes additional insight toward understanding the mechanism of SPME processes with PDMS phases.

## INTRODUCTION

Solid-phase microextraction is an organics extraction method based on quantitation of analytes sorbed on a polymeric phase, often coated on a glass fiber, in contact with water or the headspace above the aqueous phase. Since the introduction of SPME as a quantitative analytical technique by Arthur and Pawliszyn (1990) more than a decade ago, a large amount of data has been obtained concerning the fundamental mechanisms governing the SPME processes and potential applications of SPME in a variety of research areas (Pawliszyn 1997, 1999, Heringa and Hermens 2003, Mayer *et al.* 2003). The success of SPME can be attributed to its simplicity of use, combination of extraction and concentration in a single step, relatively short sample processing times, minimal solvent use, and cost effectiveness.

Successful development and implementation of a robust SPME-based method are strongly dependent upon a thorough understanding of the factors dictating the distribution of analytes between the SPME sorbent phase and sample matrix. Many SPME-based methods have been developed for specific sample matrices only; therefore, their usefulness is limited. A more universal approach is to employ the coefficient of distribution ($K_f$) of an analyte between the sorbent phase and water for quantitation, with additional considerations of matrix effects if necessary. Consequently, accurate determination of $K_f$ values becomes a critical step toward the development of a robust SPME-based method. While $K_f$ values for organic compounds with low hydrophobicity are relatively easy to determine with precision,

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quantifying $K_f$ values for very hydrophobic organic compounds (VHOCs) has remained a challenge to analytical chemists. In addition, determination of $K_f$ has been hindered by uncertainties regarding the mechanisms of the SPME process, highlighted by the ongoing vigorous debate over whether absorption or adsorption is the primary SPME sorption process (Yang *et al.* 1998, Yang *et al.* 1998, Hawthorne *et al.* 2000, Poerschmann *et al.* 2000, Vaes *et al.* 2000).

One of our goals is to utilize the SPME technology in field sampling of VHOCs in oceanic environments, a critical compartment for regional and global dispersal and transport of VHOCs. This objective requires calibration of the SPME process for a large number of analytes, and thus their associated $K_f$ values. To accomplish this goal, a slow-stirring system (Figure 1) was employed to calibrate a large set of PDMS-coated fibers for selected polychlorinated biphenyls (PCBs) and chlorinated pesticides (including *o*,*p*'- and *p*,*p*'-DDT, DDD, and DDE). These compounds normally are measured in southern California ocean monitoring programs, such as a recent regional survey (Noblet *et al.* 2002). The 100 µm PDMS phase was chosen to maximize the sensitivity of the sampling method. Several studies calibrated PDMS-coated fibers for selected PCB congeners (Potter and Pawliszyn 1994, Yang *et al.* 1998, Yang *et al.* 1998, Mayer *et al.* 2000, Poerschmann *et al.* 2000, Paschke and Popp 2003), but $K_f$ values varied substantially for different coating thicknesses,

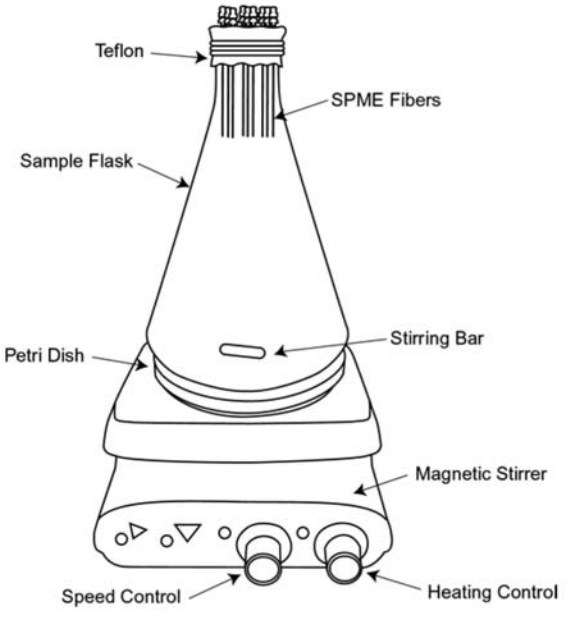


**Figure 1. Schematic of the SPME experimental setup.**

even when the same extraction procedures were employed. Since SPME performance is a function of both fiber thickness and extraction procedure, a further calibration of the 100 µm PDMS-coated fiber was warranted for our unique purposes.

## Theoretical Background

For the convenience of discussion, the analyte under consideration is assumed to be present initially in the aqueous phase. Although this assumption does not affect the generality of the conclusions derived herein, it is particularly suitable for understanding the SPME sorption processes for VHOCs as the vapor pressures of VHOCs are extremely low at room temperature. If SPME experiments are conducted in a closed system, composed of the sorbent phase, water, and headspace only and free of matrix interferences, the total amount ($N_0$) of the analyte upon completion of SPME can be expressed as:

$$N_0 = N_f + N_w + N_h \qquad (1)$$

where $N_f$, $N_w$, and $N_h$ are the amounts of the analyte in the sorbent phase, water, and headspace, respectively. An equation used to relate $N_f$ with the initial analyte concentration ($C_w^0$) can be derived from Equation (1) (Zeng and Noblet 2002):

$$N_f = \frac{K_f V_f (V_w + K'_H V_h)}{K_f V_f + V_w + K'_H V_h} C_w^0 \qquad (2)$$

where $V_f$, $V_w$, and $V_h$ are the volumes of the sorbent phase, water, and headspace, respectively, and $K'_H$ is the dimensionless Henry's Law constant. Most initial efforts for the development and applications of SPME-based methods were dedicated to volatile organic compounds (VOCs), because of the apparent benefits of using SPME with this group of chemicals. VOCs have low hydrophobicity, and therefore low $K_f$ values. Commercially available SPME devices usually have sorbent coating volumes less than 1 µL with $K_f$ values less than 100 for VOCs. Hence, use of a moderate sample volume (e.g., ~10 mL) could easily satisfy $V_w >> K_f V_f$, resulting in the simplification of Equation (2) to $N_f = K_f V_f C_w^0$ regardless of whether matrix effects are significant. With this simplified equation, the concentrations of VOCs could be determined conveniently whether the aqueous phase or the headspace is sampled with SPME devices.

In the case of VHOCs, the Henry's Law constant is small so that $K_f V_f \approx V_w >> K_H' V_h$ if the headspace volume is comparable to the sample volume. Therefore, Equation (2) becomes

$$N_f = \frac{K_f V_f V_w}{K_f V_f + V_w} C_w^0 = \frac{K_f V_f}{K_f V_f + V_w} N_0 \qquad (3)$$

Apparently, SPME measurements of VHOCs are dependent on calibration of $K_f V_f$ or $K_f$ if the sorbent coating volume is known. For complex samples, matrix effects must be accounted for. For example, an additional term (defined as matrix sorption term, $\theta$) related to interfering sorbent phases was proposed to be included in the sample volume in Equation (3), in order to correctly calculate the analyte concentration (Zeng and Noblet 2002).

Two general calibration methods have been employed to determine $K_f V_f$ values. The first method is a static SPME within a closed system. The following equation or equivalent was derived to calculate $K_f V_f$ (Poerschmann *et al.* 2000, Paschke and Popp 2003):

$$K_f V_f = \frac{N_f V_w}{C_w^0 V_w - N_f} \qquad (4)$$

One apparent drawback with this method is that large measurement errors may occur if the analyte amount ($N_f$) in the sorbent phase is approaching the initial analyte amount ($C_w^0 V_w$), i.e., the amount of the analyte in the sample matrix is severely depleted upon completion of SPME. This could occur with VHOCs if a small sample volume is used. To overcome this drawback, Mayer *et al.* (2000) proposed a slightly different static SPME strategy. They prepared a series of samples with the same analyte concentration, and added different amounts of PDMS-coated fibers to the samples to obtain varying PDMS-to-water volume ratios. Subsamples were collected into 12 mL vials and extracted with conventional SPME to determine the analyte concentrations. A reference sample without addition of PDMS-coated fibers was also analyzed. The ratio ($C_{relative}$) of the analyte concentrations in the treated and reference samples was related to the ratio ($V_f/V_w$) of the volumes of the PDMS coating and water via the following equation (Mayer *et al.* 2000):

$$C_{relative} = \frac{1}{1 + 10^{\log(K_f)}(V_f / V_w)} \qquad (5)$$

A nonlinear regression between $C_{relative}$ and $V_f/V_w$ yields the distribution coefficient $K_f$. The advantage of this approach is that the extent of depletion of the analyte could be adjusted to an optimal range by varying the amount of PDMS-coated fibers added to the samples. In addition, $K_f$ was determined with multiple analyte concentration points, leading to enhanced applicability of $K_f$ within a broad concentration range.

The second calibration method is dynamic SPME in which a constant analyte concentration is maintained by an external supply source (via a flow-through strategy) so that losses of analytes to non-SPME sorbent phases, and consequently matrix effects, can be disregarded (Poerschmann *et al.* 2000, Shurmer and Pawliszyn 2000). In this approach, mass balance no longer holds, and $K_f$ is calculated directly from its definition, $K_f = C_f/C_w$. However, the analyte concentration, $C_w$, in the sample needs to be determined by a separate analytical protocol, typically a liquid-liquid extraction method. Therefore, the accuracy of the $K_f$ values is subject also to the performance of a non-SPME method.

In this study, a static SPME strategy was adopted with a large sample volume (1.6 L) and multiple SPME devices. In addition, the glassware walls and stirring bar surface were treated as two non-SPME sorbent phases to improve the quality of the calibrated $K_f$ values. As a result of mass balance, Equation (1) can be modified to:

$$N_0 = N_w + \sum_{i=1}^{n} N_f(i) + \sum_{i'=1}^{n'} N_{sb}(i') \qquad (6)$$

where $N_f(i)$ is the amount of the analyte sorbed on the $i$th SPME device; $n$ the total number of SPME devices; $N_{sb}(i')$ the amount of the analyte sorbed on the $i'$th non-SPME sorbent phase; and $n'$ the number of non-SPME sorbent phases. Using the same procedure described previously (Zeng and Noblet 2002), the amount of the analyte sorbed on the $j$th SPME device is given by:

$$N_f(j) = \frac{K_f V_f}{K_f V_f + V_w + \theta} (N_0 - \sum_{i \neq j}^{n} N_f(i)) \qquad (7)$$

where $\theta$ is defined as a matrix sorption term, which accounts for the $N_{sb}$ term in Equation 6. The $\theta$ term will be further discussed below. If $S$ is defined as the slope of the linear regression of $N_f(j)$ versus ($N_0$ - $\sum_{i \neq j}^{n} N_f(i)$), the following equation can be derived:

$$S = \frac{K_f V_f}{K_f V_f + V_w + \theta}$$

or

$$K_f V_f = \frac{S(V_w + \theta)}{1 - S} \quad (8)$$

Apparently, the present analytical method is developed directly from the linearity between the analyte amount retained by an SPME device and the initial analyte amount (subtracting the analyte amounts retained by all other SPME devices). Linear regression over a large concentration range (2 to 50 ng/L in the present study) ensures the wide-range applicability of the measured $K_f$ values. In addition, the use of multiple SPME devices in one calibration system allows the calibration data to be analyzed statistically. To estimate the value of $\theta$ in a given system, we rewrite $\theta$ as (Zeng and Noblet 2002):

$$\theta = \sum_{i=1}^{n'} K_{sb}^{i} m_{sb}^{i} \quad (9)$$

where *n'* is the number of non-SPME sorbent phases present in the system; $K_{sb}^{i}$ is the distribution coefficient of the analyte between the *i*th non-SPME sorbent phase and water; and $m_{sb}^{i}$ is the apparent mass of the *i*th non-SPME sorbent phase. By definition, $K_{sb}^{i} = C_{sb}^{i} / C_w$, where $C_{sb}^{i}$ is the concentration of the analyte in the *i*th non-SPME sorbent phase. By substituting this relationship into Equation (9) and noting $N_{sb}(i) = C_{sb}^{i} m_{sb}^{i}$, the following equation can be derived:

$$\sum_{i=1}^{n'} N_{sb}(i) = \theta\, C_w \quad (10)$$

Therefore, $\theta$ can be estimated from the linear regression of $\sum_{i=1}^{n'} N_{sb}(i)$ versus $C_w$ with $\sum_{i=1}^{n'} N_{sb}(i)$ being determined with any non-SPME method. In the present study, the glassware walls and stirring bars were the non-SPME sorbent phases. Headspace was deemed an insignificant phase for the target analytes under investigation.

## Methods

### Study Design

This study was conducted in three incremental steps. First, a series of seawater spiked with the same amount of the target analytes were extracted for various time durations to establish the kinetics of the SPME process. Second, SPME experiments were conducted at the equilibrium state derived from the kinetics experiments and were used to determine $K_f V_f$ values for the target analytes. Finally, the value of the matrix sorption term, $\theta$, for each analyte was estimated from non-SPME experiments and used to correct for interferences with the determination of $K_f V_f$ values from container walls and stir bar surface.

### Apparatus and Materials

SPME devices with 100 µm PDMS coating were purchased from Supelco (Bellefonte, PA). Each SPME device was washed with hexane and heated at 280°C under helium stream (on a gas chromatography (GC) injection port) for 1 h prior to initial use or after each injection. Conditioned SPME devices were stored in a freezer at –20°C if not used immediately. Glass Erlemeyer flasks with a volume of ~1.7 L were obtained from Corning (Corning, NY). They were washed with detergent and tap water, rinsed with deionized water, kilned at 420°C for at least 4 h. Immediately prior to use, each flask was silanized with a solution of 15% dimethyldichlorosilane in toluene (Aldrich Chemical, Milwaukee, WI) for ~1 min. Silanized flasks were rinsed twice with toluene and three times with methanol, stored at 100°C, and rinsed with deionized water. Teflon®-coated stirring bars (Corning, Corning, NY) were rinsed with deionized water, sonicated in methylene chloride for 20 min, and dried at 100°C. Sodium azide was obtained from Mallinckrodt Baker (Phillipsburg, NJ).

Custom-made mixtures of PCB congeners (20 µg/mL each in hexane:isooctane (98:2)) and chlorinated pesticides (100 µg/mL each in acetone) were supplied by AccuStandards (New Haven, CT). OPTIMA grade acetone and hexane were purchased from Fisher Scientific (Pittsburgh, PA) and used as supplied. Sand-filtered seawater was collected from an off-shore intake of Southern California Edison (Redondo Beach, CA) and used without any treatment.

### SPME Procedures

Standard solutions containing all target analytes were mixed with acetone to make up spiking solutions (in 0.5 mL acetone) with various analyte concentrations. Each Erlemeyer flask was filled with 1.6 L of seawater and spiked with a spiking solution. One stirring bar was placed in the flask. The antibiotic agent, sodium azide, was added to the flask if the experiment was to be conducted for longer than 4

d. A silanized Teflon® sheet was bound to the opening of the flask with rubber bands to make the system airtight. Upon rinse with hexane, multiple SPME devices were pierced through the Teflon sheet and into the spiked seawater. The PDMS-coated fibers were protracted and exposed to the spiked seawater. The flask was placed on a Corning stirrer (Corning, NY). To minimize heat transfer from the stirrer motor to the flask, a 150 x 15 mm polystyrene Petri dish with lids was placed between the stirrer and the flask. All experiments were conducted at ambient temperature 22±2°C. At the end of the extraction, the PDMS-coated fibers were removed with care from the flask and dipped briefly into deionized water to remove residual salt from the seawater. The fibers then were shaken rigorously to remove any water residues before being retracted into the needle sleeves. Analytes sorbed on SPME devices were thermally desorbed into a programmed injector on a specified gas chromatography/mass spectrometry (GC/MS) instrument. SPME devices not analyzed immediately were stored at –20°C.

For uptake kinetics experiments, three SPME devices were used simultaneously in one flask. SPME extraction times were 1, 2, 4, 8, and 16 h and 1, 2, 4, 6, 8, 12, 16, and 24 d. Two agitation speeds, 380 and 870 revolutions per minute (rpm), were tested. For equilibrium calibration experiments, an extraction time of 12 d and an agitation speed of 870 rpm were chosen, based on the results of the kinetics experiments, to determine $K_f$ values. Nine SPME devices were placed in one flask. The calibration concentrations were 2, 5, 20, and 50 ng/L for all target analytes.

**Non-SPME Procedures**

To determine the $\theta$ values, four seawater samples (1.6 L) containing the target analytes at 100, 250, 500, and 1000 ng/L, respectively, were prepared in four Erlemeyer flasks. One stirring bar was placed in each flask and the samples were treated using the same method as those with the SPME procedures, except that no SPME devices were added. At the end of the 12-d extraction period, seawater was processed with a solid-phase extraction method (Zeng and Khan 1995), stirring bars were extracted with a roller table method (Zeng and Vista 1997), and the glassware walls were rinsed with methylene chloride and the rinsates were collected. All fractions were condensed to 1 mL using a Zymark TurboVap 500 (Zymark Corporation, Hopkinton, MA). Internal standards, PCB 30 and 205, were added to all extracts prior to instrumental analysis.

**GC/MS Analysis**

Two Varian Saturn 2000 GC/Ion Trap MS systems were used for sample analysis, labeled as GC-MS-1 and GC-MS-2. To maintain consistency, all SPME devices used in the kinetics experiments were analyzed using GC-MS-1. SPME devices from the equilibrium experiments were categorized into analytical batches 1 to 7. Devices in batches 1-4 were analyzed with GC-MS-1, and those in batches 5-7 were analyzed with GC-MS-2. The chromatographic conditions used for these two instruments basically were identical except where it was indicated. Chromatographic separation was made with 60 m ´ 0.25 mm-i.d. (0.25 µm film thickness) DB-5MS columns (J&W Scientific, Folsom, CA). Column temperature was programmed from 80°C (hold for 1 min) to 176°C at a rate of 8°C/min, followed by a ramp to 230°C at a rate of 1.5°C/min, and finally increased to 290°C (5°C/min) where it was held for 21 min. Both SPME and direct solvent injections were conducted with a split/splitless mode (split initially, splitless 0.01 min after injection, and split again 2.5 min after injection). The injector temperature was programmed from 100°C (held for 0.05 min) to 280°C with the maximum ramping rate (~100°C/min) and held for 40 min at 280°C. Under these chromatographic conditions, slightly different retention times were obtained on the two instruments for the same target analytes. To reduce the retention time difference, the flow rate was set at 1.0 and 1.3 mL/min for GC-MS-1 and GC-MS-2, respectively. All the extracts obtained from the non-SPME procedures were analyzed with GC-MS-1.

Mass spectra were acquired with the electron ionization mode. Mass spectra were acquired from 100 to 504 *m*/*z* with a scan time of 0.7 scans per second and an emission current of 15 mamps. Within this range, the ion storage level was 79 and the ionization time factor was 100%. The ionization time factor was 10% outside this range. Electron multiplier voltage was 1900-2000 eV for GC-MS-1 and 1500-1600 eV for GC-MS-2, because a newer electron multiplier was installed in GC-MS-2. Temperatures of the ion trap, manifold, and transfer line were set at 200, 80, and 280°C, respectively. To ensure the linearity of the instrument performance, calibration standard solutions containing all the target analytes at 50, 100, 250, 500, 1000, and 2000

ng/mL with internal standards at 500 ng/mL were analyzed frequently throughout the study. Linear calibration curves were always obtained for all target analytes.

**Data Analysis**

*Normalization of MS Responses*. Calibration is a necessary step in instrumental analysis in order to account for the variability in instrument performance. In a regular GC/MS analysis, instrument variability can be corrected intrinsically by the addition of internal standards into the calibration standard solutions and samples. With SPME, however, internal calibration is possible only if both the target analyte and its deuterated counterpart are analyzed simultaneously. This approach faces two obstacles. First, the cost of employing deuterated standards could become extraordinary for a large number of analytes. Second, even with the use of deuterated compounds, the SPME behavior and MS responses must be assumed identical for both the undeuterated and deuterated counterparts, which remains to be fully verified. In line with these considerations, an external calibration method was used in our study.

Prior to the analysis of each batch of up to seven loaded SPME devices, 1 μL of a standard mixture containing all the target analytes at 2 μg/mL was injected into the GC/MS instrument with an autosampler. The MS responses from the direct injection of the standard solution and desorption of analytes sorbed on SPME devices were used to calculate either normalized responses for the kinetics experiments or analyte amounts for the equilibrium experiments.

*Kinetic Data*. A typical SPME process generally is believed to occur via a first-order diffusion of the target analyte across the polymeric coating-water interface. The amount ($N_f$) of the analyte sorbed on an SPME device may be related to extraction time ($t$) through the following equation (Ai 1997):

$$N_f = N_f^o\ (1 - e^{-bt}) \qquad (11)$$

where $N_f^o$ is the amount of the analyte sorbed on the device fiber at truly equilibrium state ($t \rightarrow \infty$) and $b$ is a kinetic constant related to the types of polymeric coating and analyte, as well as the sample volume (Ai 1997). In the context of sorption and desorption involved in a diffusion process, $b$ can also be regarded as the rate of desorption from the SPME sorbent phase to the aqueous phase. Apparently, Equation (11) can be rearranged to estimate the percent of equilibrium state (defined as $P_{ES}$) with finite extraction time $t$:

$$P_{ES} = 100\%\ (1 - e^{-bt}) \qquad (12)$$

Finally, if the system is not at equilibrium state when the analyte is sampled, the time factor is given by $1 - e^{-bt}$, based on a nonequilibrium model (Ai 1997). Equation (8) can be modified to

$$K_f V_f = \frac{S(V_w + \theta)}{1 - e^{-bt} - S}$$

## Results and Discussion

**Kinetics of SPME Process**

The SPME process was simulated reasonably well with a first-order diffusion model depicted by Equation (11). The correlation coefficients for the model simulation were largely about 0.7 (Table 1), indicating a fair amount of variability in the kinetic experiments. Since different PDMS-coated fibers were used at different time points in the experiments, the variability may partially reflect differences in the sorptive capacity among individual fibers.

The $N_f^o$ values increased initially and then decreased with congener number for PCBs, but $b$ essentially decreased with increasing congener number. As a result, the percent of equilibrium state ($P_{ES}$) calculated with Equation (12) at 12 d generally decreased with increasing congener number (Table 1). However, the $P_{ES}$ values at 12 d were greater than 80% for all analytes but PCB 209. In general, chlorinated pesticides reached a higher percent of equilibrium state than PCBs under the experimental conditions. In the equilibrium experiments, an extraction time of 12 d was used. Because of the moderate variability of the data set, there was no need to include the extraction time factor as indicated in Equation (13) in the determination of $K_f V_f$ values.

As stated previously, one objective of this study was to develop a feasible field sampling method based on the SPME technology. Consequently, the agitation speed was set to simulate the speed of bottom currents in the coastal ocean of southern California. A previous study obtained the near-bottom current speeds at ~5-6 cm/s around the coastal oceans off southern California (Southern California Coastal Water Research Project 1994). The agitation

**Table 1. Kinetic parameters associated with SPME processes based on Equations (11) and (12). $R^2$ is the correlation coefficient for the nonlinear regressions.**

| | $R^2$ | $N_f^{0}$ * | $b$ ($h^{-1}$) | $P_{ES}$ (%) ** |
|---|---|---|---|---|
| PCB 18 | 0.84 | 146 (6) | 0.0273 (0.0046) | 100 |
| PCB 28 | 0.71 | 195 (14) | 0.0177 (0.0050) | 99 |
| PCB 37 | 0.64 | 213 (18) | 0.0195 (0.0063) | 100 |
| PCB 44 | 0.77 | 366 (32) | 0.0096 (0.0026) | 94 |
| PCB 49 | 0.76 | 360 (33) | 0.0090 (0.0026) | 93 |
| PCB 52 | 0.76 | 352 (31) | 0.0096 (0.0027) | 94 |
| PCB 65 | 0.74 | 332 (31) | 0.0097 (0.0030) | 94 |
| PCB 66 | 0.70 | 351 (36) | 0.0098 (0.0032) | 94 |
| PCB 70 | 0.74 | 377 (38) | 0.0091 (0.0026) | 93 |
| PCB 74 | 0.74 | 335 (32) | 0.0091 (0.0027) | 93 |
| PCB 77 | 0.72 | 348 (34) | 0.0103 (0.0030) | 95 |
| PCB 81 | 0.71 | 363 (35) | 0.0099 (0.0033) | 94 |
| PCB 87 | 0.74 | 429 (49) | 0.0068 (0.0023) | 86 |
| PCB 99 | 0.73 | 372 (45) | 0.0066 (0.0023) | 85 |
| PCB 101 | 0.73 | 420 (50) | 0.0066 (0.0024) | 85 |
| PCB 105 | 0.71 | 383 (44) | 0.0074 (0.0026) | 88 |
| PCB 110 | 0.72 | 432 (50) | 0.0071 (0.0025) | 87 |
| PCB 114 | 0.71 | 344 (40) | 0.0073 (0.0027) | 88 |
| PCB 118 | 0.75 | 346 (40) | 0.0068 (0.0022) | 86 |
| PCB 119 | 0.71 | 373 (47) | 0.0068 (0.0025) | 86 |
| PCB 123 | 0.70 | 338 (42) | 0.0069 (0.0025) | 86 |
| PCB 126 | 0.69 | 366 (44) | 0.0086 (0.0029) | 92 |
| PCB 128 | 0.69 | 277 (38) | 0.0064 (0.0024) | 84 |
| PCB 138 | 0.68 | 283 (39) | 0.0063 (0.0025) | 84 |
| PCB 149 | 0.67 | 312 (45) | 0.0063 (0.0025) | 84 |
| PCB 151 | 0.67 | 338 (55) | 0.0065 (0.0024) | 85 |
| PCB 153/168 | 0.62 | 223 (33) | 0.0071 (0.0032) | 87 |
| PCB 156 | 0.73 | 246 (30) | 0.0068 (0.0023) | 86 |
| PCB 157 | 0.77 | 225 (25) | 0.0065 (0.0019) | 85 |
| PCB 158 | 0.60 | 220 (34) | 0.0079 (0.0033) | 90 |
| PCB 167 | 0.75 | 209 (26) | 0.0062 (0.0020) | 83 |
| PCB 169 | 0.76 | 197 (21) | 0.0073 (0.0020) | 88 |
| PCB 170 | 0.69 | 128 (18) | 0.0063 (0.0023) | 84 |
| PCB 177 | 0.64 | 159 (25) | 0.0061 (0.0027) | 83 |
| PCB 180 | 0.72 | 137 (19) | 0.0060 (0.0021) | 82 |
| PCB 183 | 0.65 | 134 (23) | 0.0063 (0.0024) | 84 |
| PCB 187 | 0.66 | 152 (26) | 0.0062 (0.0024) | 83 |
| PCB 189 | 0.73 | 122 (16) | 0.0061 (0.0020) | 83 |
| PCB 194 | 0.72 | 68 (9) | 0.0060 (0.0018) | 82 |
| PCB 200 | 0.66 | 63 (9) | 0.0068 (0.0024) | 86 |
| PCB 201 | 0.68 | 72 (10) | 0.0063 (0.0023) | 84 |
| PCB 206 | 0.73 | 37 (4) | 0.0066 (0.0018) | 85 |
| PCB 209 | 0.56 | 25 (6) | 0.0038 (0.0018) | 66 |
| Aldrin | 0.72 | 428 (52) | 0.0068 (0.0024) | 86 |
| -Chlordane | 0.74 | 356 (33) | 0.0103 (0.0028) | 95 |
| -Chlordane | 0.74 | 379 (38) | 0.0094 (0.0027) | 93 |
| Chlordene | 0.80 | 274 (21) | 0.0106 (0.0024) | 95 |
| Chloropyrifos | 0.58 | 63 (4) | 0.1144 (0.0337) | 100 |
| Diazinon | 0.21 | 10 (1) | 0.3589 (0.1187) | 100 |
| Dieldrin | 0.77 | 129 (6) | 0.0469 (0.0091) | 100 |
| Endrin | 0.55 | 58 (4) | 0.0775 (0.0233) | 100 |
| *cis*-Nonachlor | 0.72 | 331 (32) | 0.0108 (0.0032) | 96 |
| *trans*-Nonachlor | 0.72 | 438 (51) | 0.0081 (0.0026) | 90 |
| Oxychlordane | 0.75 | 332 (29) | 0.0102 (0.0030) | 95 |
| *o,p'*-DDD | 0.76 | 314 (25) | 0.0119 (0.0030) | 97 |
| *p,p'*-DDD | 0.75 | 275 (19) | 0.0160 (0.0039) | 99 |
| *o,p'*-DDE | 0.67 | 439 (58) | 0.0075 (0.0029) | 89 |
| *p,p'*-DDE | 0.68 | 435 (62) | 0.0070 (0.0026) | 87 |
| *o,p'*-DDT | 0.65 | 353 (53) | 0.0065 (0.0028) | 84 |
| *p,p'*-DDT | 0.64 | 407 (59) | 0.0078 (0.0031) | 89 |

* Mass spectral abundances of sorbed analytes normalized to those from standard solvent injection.
** Calculated at the extraction time of 12 d.

velocity in water, labeled as $u(r)$, could be estimated through the following equation (Pawliszyn 1997):

$$u(r) = 0.575pNR^2 \frac{1}{r} \text{ for } r > 0.74R \qquad (14)$$

where $R$ is the radius of the stir bar; $N$ is the revolutions per second; and $r$ is the distance between the center of the container and the PDMS-coated fiber. The agitation velocity in our experiments estimated from Equation (14) was about 4 cm/s. Note that Equation (14) is applicable to cylindrical containers, whereas the flasks used in our experiments are pear-shaped. As the PDMS-coated fibers were positioned at the smaller end of the flask (Figure 1), the agitation velocity based on Equation (14) was likely underestimated. Therefore, the actual agitation velocity is considered slightly greater than 4 cm/s, but still much slower than those normally used by other researchers. One negative consequence of using a slow-stirring procedure with a large sample volume (1.6 L) is the extended experimental time needed to reach equilibrium. This could allow bacteria to grow, which could biodegrade the analytes. We observed that both *o,p'*- and *p,p'*-DDT began to suffer losses after more than 4 d of SPME experiments without the antibiotic agent (sodium azide) added. Therefore, it was necessary to add the antibiotic agent to samples subject to SPME of equal to or longer than 4 d.

In several previous studies, the equilibrium time for SPME of PCBs varied from several hours (Yang *et al.* 1998, Yang *et al.* 1998) to several weeks (Mayer *et al.* 2000), depending mainly on the effective agitation velocity around the SPME fiber. As indicated by Equation (14), the agitation velocity is disproportional to the distance between the SPME fiber and the center of the container. Hence, the agitation velocity likely decreases with increasing sample size. It is also beneficial to use stirring bars with a large radius if a large sample container is employed.

### Determination of $K_fV_f$ Values

Table 2 summarizes the data acquired from the calibration of the 100 μm PDMS-coated fibers. The log $K_f$ values were calculated from the $K_fV_f$ data and the $V_f$ value of 0.612 μL provided by Supelco. The five-point calibration (including the origin) procedure employed to obtain $K_fV_f$ using

Equation (7) appeared valid, as signaled by generally high $r^2$ values for a total of 60 analytes. The linear regressions to estimate $\theta$ values for all the analytes using Equation (10) were also reasonably sound as an average $r^2$ value was 0.88±0.14.

An unexpected occurrence is the significant difference between the $K_fV_f$ values obtained with two seemingly identical GC/MS systems. The target analytes that do not have significant different $K_fV_f$ values obtained with GC-MS-1 and GC-MS-2 are PCB 194, PCB 206, PCB 209, endrin, and *o*,*p*'-DDT. Except for *o*,*p*'-DDT, $K_fV_f$ values for these compounds are all unexpectedly low (Table 2). As the SPME devices were randomly selected from a large pool purchased on different days, variability in the sorption property of the commercial PDMS-coated fibers was ruled out as the significant source of the difference. The Corning stirrers were maintained at the same operational mode during the entire experimental period and were chosen randomly for specific testing batches. Hence, agitation speed was also ruled out as the main reason for the difference. In analyses of the analytes desorbed from the PDMS-coated fibers, mass spectral abundances (area counts) from analysis of solvent-prepared standards were used to normalize those from the PDMS-coated fibers. It appears that the two GC/MS instruments had different responses to the mass spectral abundances from the injection of solvent-prepared standards, compared to those from desorption of analytes sorbed in the PDMS phase. This caused a substantial discrepancy between the normalized area counts obtained with the two GC/MS instruments for the same level of SPME exposure. However, the mechanism behind the discrepancy remains to be identified.

Regardless of the difference between the two groups of calibration data, the correlation between log $K_f$ and log $K_{ow}$ was similar for both groups (Figure 2). Log $K_f$ increases with log $K_{ow}$ initially, but reaches a plateau at log $K_{ow} \approx 6.5$, and then decreases as log $K_{ow}$ continues to rise. To better demonstrate the dependence of log $K_f$ on log $K_{ow}$, the PCB congeners in Group 1 (analytical batches 1-4) were grouped based on the number of chlorines (homolog) on the benzene rings. Log $K_f$ increases with increasing log $K_{ow}$ for homologs 3-4 and 5, but decreases with increasing log $K_{ow}$ for homologs 6 and 7-10 (Figure 3). Doong and Chang (2000) also reported a linear correlation between $K_f$ and $K_{ow}$ for polycyclic aromatic hydrocarbon (PAH) compounds with log $K_{ow}$ less than six, but obtained a negative correlation for five- and six-ring PAHs.

In general, the quality of linear regressions with Group 1 is better than that with Group 2 (Table 2). Therefore, the calibration data for Group 1 will be used in the following section to compare with previously acquired data in the literature.

**Comparison with Previous Studies**

A number of studies obtained $K_f$ values for selected PCB congeners and DDT compounds with PDMS-coated fibers (Table 3). Apparently, a large variability in $K_f$ values has been obtained with different experimental procedures, PDMS coating thickness, and researchers. For example, Mayer *et al.* (2000) obtained higher $K_f$ values with increasing $K_{ow}$ values with a 6-wk extraction time compared to a 3-d extraction using a 15 μm coating. Sufficient equilibrium time was cited as an important factor to achieve appropriate $K_f$ values. Poreschmann *et al.* (2000) acquired higher $K_f$ values with a larger sample volume (250 mL) than with a smaller one (4 mL) using a static SPME method. They were able to achieve even higher $K_f$ values using a dynamic SPME method in which the analyte concentrations were maintained constant by an external supply source. More recently, Paschke and Popp (2003) used a static SPME method to determine $K_f$ on 7 and and 10 μm PDMS-coated fibers in an Erlenmeyer flask (with a sample size of 480 mL). The $K_f$ values for PCB congeners on the 7 μm PDMS-coated fibers essentially increase with increasing $K_{ow}$ values. The $K_f$ values for PCB congeners on the 10 μm PDMS-coated fibers also increase initially with increasing $K_{ow}$ values, but top out at log $K_{ow} \approx 6.9$ and then decrease slightly afterwards (Table 3). The log $K_f$ values obtained in the present study using a 100 μm PDMS coating increase with increasing log $K_{ow}$ up to log $K_{ow} \approx 6.5$, and decreases drastically afterwards (Figure 2). The log $K_f$ value for *p*,*p*'-DDE (5.74±0.07) determined in the present study is similar to those acquired by Meyer *et al.* (2000) using a 15 μm PDMS coating (5.73±0.09 and 5.88±0.05 for extractions times of 3 d and 6 wks, respectively), but quite distinct from those obtained by Paschke and Popp (2003) for 7 μm (5.39) and 100 μm (5.26) PDMS coatings. Our log $K_f$ values of *p*,*p*'-DDD and *p*, *p*'-DDT were also inconsistent with those meas-

**Table 2. Equilibrium sorption properties of polychlorinated biphenyls (PCBs) and chlorinated pesticides on poly(dimethylsiloxane) coated fibers. $r^2$ is the correlation coefficient for linear regressions on Equation (7). The number of fibers (samples) for Groups 1 and 2 were 26 and 25, respectively. Water volume was 1.6 L for all the experiments.**

| | $r^2$ | | | $K_f V_f$ [b] ($\mu L \times 10^{-4}$) | | log $K_f$ [c] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Group 1 | Group 2 | $\theta$ (L) [a] | Group 1 | Group 2 | Group 1 | Group 2 | log $K_{ow}$ [d] | $p$ [e] |
| PCB 18 | 0.97 (0.03) | 0.97 (0.02) | 0.12 (0.00) | 7.93 (1.15) | 5.67 (1.28) | 5.11 (0.06) | 4.96 (0.09) | 5.24 | 0.000 |
| PCB 28 | 0.97 (0.03) | 0.96 (0.03) | 0.36 (0.06) | 10.65 (1.69) | 8.22 (2.20) | 5.24 (0.07) | 5.11 (0.11) | 5.67 | 0.000 |
| PCB 37 | 0.94 (0.03) | 0.95 (0.04) | 0.54 (0.16) | 12.28 (3.07) | 8.57 (2.66) | 5.29 (0.10) | 5.13 (0.13) | 5.83 | 0.000 |
| PCB 44 | 0.96 (0.03) | 0.94 (0.03) | 0.46 (0.01) | 19.05 (2.61) | 12.80 (4.87) | 5.49 (0.06) | 5.29 (0.15) | 5.75 | 0.000 |
| PCB 49 | 0.96 (0.03) | 0.94 (0.03) | 0.55 (0.10) | 20.26 (2.94) | 13.31 (4.75) | 5.52 (0.06) | 5.31 (0.14) | 5.85 | 0.000 |
| PCB 52 | 0.96 (0.03) | 0.94 (0.02) | 0.45 (0.05) | 19.30 (2.93) | 12.79 (4.38) | 5.49 (0.06) | 5.30 (0.14) | 5.84 | 0.000 |
| PCB 65 | 0.96 (0.03) | 0.92 (0.05) | 0.48 (0.08) | 23.72 (4.04) | 14.60 (5.23) | 5.58 (0.07) | 5.35 (0.14) | 5.86 | 0.000 |
| PCB 66 | 0.95 (0.05) | 0.92 (0.03) | 0.96 (0.10) | 23.11 (3.48) | 17.49 (7.83) | 5.57 (0.06) | 5.42 (0.17) | 6.20 | 0.002 |
| PCB 70 | 0.96 (0.04) | 0.93 (0.03) | 0.85 (0.13) | 20.40 (2.81) | 15.54 (6.50) | 5.52 (0.06) | 5.37 (0.16) | 6.20 | 0.001 |
| PCB 74 | 0.95 (0.06) | 0.93 (0.03) | 0.96 (0.24) | 20.26 (2.75) | 15.69 (6.24) | 5.52 (0.06) | 5.38 (0.15) | 6.20 | 0.001 |
| PCB 77 | 0.94 (0.05) | 0.91 (0.06) | 3.65 (0.04) | 39.22 (3.80) | 32.91 (15.39) | 5.80 (0.04) | 5.69 (0.18) | 6.36 | 0.048 |
| PCB 81 | 0.96 (0.04) | 0.88 (0.13) | 1.24 (0.09) | 25.50 (2.85) | 16.49 (8.32) | 5.62 (0.05) | 5.38 (0.21) | 6.36 | 0.000 |
| PCB 87 | 0.94 (0.05) | 0.89 (0.07) | 1.57 (0.29) | 23.75 (3.33) | 17.76 (8.93) | 5.58 (0.06) | 5.42 (0.20) | 6.29 | 0.002 |
| PCB 99 | 0.93 (0.06) | 0.88 (0.09) | 1.89 (0.53) | 22.80 (3.17) | 17.19 (8.19) | 5.57 (0.06) | 5.41 (0.19) | 6.39 | 0.002 |
| PCB 101 | 0.94 (0.05) | 0.89 (0.08) | 1.67 (0.39) | 25.11 (37.60) | 18.20 (8.63) | 5.61 (0.07) | 5.43 (0.19) | 6.38 | 0.001 |
| PCB 105 | 0.94 (0.04) | 0.90 (0.08) | 3.63 (0.68) | 33.58 (4.93) | 21.33 (6.26) | 5.73 (0.06) | 5.53 (0.12) | 6.65 | 0.000 |
| PCB 110 | 0.94 (0.05) | 0.89 (0.09) | 1.52 (0.31) | 23.24 (3.21) | 16.24 (7.56) | 5.58 (0.06) | 5.38 (0.19) | 6.48 | 0.000 |
| PCB 114 | 0.92 (0.07) | 0.88 (0.09) | 3.62 (0.70) | 29.92 (4.15) | 20.00 (8.18) | 5.69 (0.06) | 5.48 (0.16) | 6.65 | 0.000 |
| PCB 118 | 0.92 (0.07) | 0.88 (0.09) | 3.63 (0.69) | 28.66 (3.36) | 19.46 (6.68) | 5.67 (0.05) | 5.48 (0.13) | 6.74 | 0.000 |
| PCB 119 | 0.92 (0.07) | 0.84 (0.13) | 1.95 (0.47) | 23.07 (3.44) | 17.34 (8.85) | 5.57 (0.07) | 5.40 (0.21) | 6.58 | 0.004 |
| PCB 123 | 0.90 (0.10) | 0.87 (0.10) | 3.77 (0.62) | 28.09 (4.27) | 21.34 (10.87) | 5.66 (0.07) | 5.50 (0.20) | 6.74 | 0.005 |
| PCB 126 | 0.93 (0.04) | 0.90 (0.04) | 3.96 (0.59) | 32.85 (4.72) | 27.19 (12.78) | 5.73 (0.06) | 5.61 (0.18) | 6.89 | 0.004 |
| PCB 128 | 0.93 (0.06) | 0.88 (0.11) | 4.50 (0.41) | 20.96 (5.20) | 11.92 (4.07) | 5.52 (0.10) | 5.27 (0.14) | 6.74 | 0.000 |
| PCB 138 | 0.92 (0.06) | 0.89 (0.09) | 4.42 (0.52) | 19.20 (4.11) | 14.31 (6.73) | 5.49 (0.09) | 5.32 (0.20) | 6.83 | 0.003 |
| PCB 149 | 0.93 (0.05) | 0.87 (0.12) | 4.16 (0.44) | 23.10 (5.35) | 16.44 (7.98) | 5.57 (0.10) | 5.38 (0.21) | 6.67 | 0.001 |
| PCB 151 | 0.93 (0.06) | 0.87 (0.13) | 4.11 (0.53) | 27.25 (6.98) | 18.62 (9.33) | 5.64 (0.11) | 5.43 (0.21) | 6.64 | 0.001 |
| PCB 153/168 | 0.79 (0.15) | 0.84 (0.12) | 3.74 (0.54) | 17.59 (4.07) | 12.46 (6.16) | 5.45 (0.10) | 5.26 (0.21) | 6.92 | 0.001 |
| PCB 156 | 0.91 (0.06) | 0.85 (0.09) | 4.17 (0.54) | 17.12 (3.83) | 13.31 (6.70) | 5.44 (0.09) | 5.29 (0.20) | 7.18 | 0.016 |
| PCB 157 | 0.91 (0.05) | 0.87 (0.12) | 4.11 (0.41) | 15.70 (3.55) | 11.74 (4.97) | 5.40 (0.10) | 5.25 (0.19) | 7.18 | 0.002 |
| PCB 158 | 0.93 (0.04) | 0.82 (0.12) | 4.46 (0.61) | 20.69 (4.88) | 14.60 (7.05) | 5.52 (0.10) | 5.33 (0.20) | 7.02 | 0.001 |
| PCB 167 | 0.92 (0.05) | 0.84 (0.13) | 4.13 (0.51) | 14.53 (3.10) | 10.68 (4.68) | 5.37 (0.09) | 5.20 (0.18) | 7.27 | 0.001 |
| PCB 169 | 0.90 (0.05 | 0.86 (0.11) | 4.00 (0.45) | 14.37 (2.99) | 11.54 (5.11) | 5.36 (0.09) | 5.24 (0.18) | 7.42 | 0.019 |
| PCB170 | 0.92 (0.04) | 0.87 (0.11) | 4.07 (0.15) | 6.69 (1.97) | 4.89 (1.92) | 5.02 (0.13) | 4.87 (0.19) | 7.27 | 0.001 |
| PCB 177 | 0.93 (0.05) | 0.88 (0.10) | 4.47 (0.12) | 9.04 (2.68) | 6.34 (2.87) | 5.15 (0.12) | 4.97 (0.21) | 7.08 | 0.001 |
| PCB 180 | 0.92 (0.05) | 0.84 (0.15) | 4.19 (0.35) | 7.35 (1.96) | 5.49 (2.07) | 5.07 (0.11) | 4.92 (0.18) | 7.36 | 0.002 |
| PCB 183 | 0.93 (0.04) | 0.84 (0.14) | 4.21 (0.17) | 7.74 (2.21) | 5.82 (2.60) | 5.09 (0.12) | 4.93 (0.20) | 7.20 | 0.007 |
| PCB 187 | 0.92 (0.05) | 0.84 (0.15) | 4.32 (0.16) | 8.85 (2.48) | 6.42 (2.97) | 5.14 (0.12) | 4.97 (0.21) | 7.17 | 0.003 |
| PCB 189 | 0.89 (0.06) | 0.85 (0.12) | 3.78 (0.30) | 6.34 (1.48) | 4.67 (1.81) | 5.00 (0.10) | 4.85 (0.18) | 7.71 | 0.001 |
| PCB 194 | 0.87 (0.19) | 0.81 (0.22) | 3.95 (0.34) | 3.23 (1.04) | 3.23 (1.92) | 4.70 (0.14) | 4.66 (0.24) | 7.80 | 0.991 |
| PCB 200 | 0.66 (0.24) | 0.85 (0.17) | 4.00 (0.11) | 5.06 (2.64) | 2.85 (0.99) | 4.87 (0.19) | 4.64 (0.17) | 7.27 | 0.000 |
| PCB 201 | 0.89 (0.07) | 0.85 (0.22) | 3.82 (0.13) | 3.73 (1.16) | 2.57 (0.93) | 4.77 (0.12) | 4.59 (0.17) | 7.62 | 0.000 |
| PCB 206 | 0.73 (0.26) | 0.88 (0.09) | 3.54 (0.11) | 1.88 (0.71) | 1.50 (0.80) | 4.46 (0.17) | 4.33 (0.23) | 8.09 | 0.071 |
| PCB 209 | 0.78 (0.24) | 0.90 (0.11) | 4.55 (0.26) | 1.25 (0.58) | 0.94 (78) | 4.27 (0.20) | 4.06 (0.33) | 8.18 | 0.109 |
| Aldrin | 0.97 (0.03) | 0.94 (0.06) | 2.18 (0.96) | 52.85 (13.47) | 40.79 (18.69) | 5.92 (0.11) | 5.79 (0.17) | --- | 0.011 |
| $\alpha$-Chlordane | 0.97 (0.02) | 0.93 (0.05) | 0.33 (0.01) | 21.17 (2.64) | 12.32 (5.40) | 5.54 (0.06) | 5.27 (0.17) | --- | 0.000 |
| $\gamma$-Chlordane | 0.96 (0.02) | 0.93 (0.06) | 0.44 (0.01) | 23.75 (2.84) | 15.51 (8.64) | 5.59 (0.05) | 5.35 (0.22) | --- | 0.000 |
| Chlordene | 0.97 (0.03) | 0.91 (0.06) | 1.12 (0.23) | 36.62 (8.49) | 20.27 (7.58) | 5.77 (0.09) | 5.49 (0.15) | --- | 0.000 |
| Chloropyrifos | 0.97 (0.04) | 0.91 (0.06) | 0.00 (0.00) | 2.73 (0.48) | 3.41 (1.22) | 4.64 (0.07) | 4.72 (0.15) | --- | 0.012 |
| Diazinon | 0.95 (0.04) | 0.93 (0.05) | 0.00 (0.00) | 0.48 (0.11) | 0.39 (0.16) | 3.88 (0.10) | 3.76 (0.20) | --- | 0.019 |
| Dieldrin | 0.98 (0.02) | 0.94 (0.05) | 0.23 (0.08) | 5.85 (0.91) | 4.61 (1.41) | 4.98 (0.07) | 4.86 (0.13) | --- | 0.001 |
| Endrin | 0.97 (0.04) | 0.84 (0.26) | 0.10 (0.02) | 2.58 (0.61) | 2.72 (0.62) | 4.61 (0.10) | 4.64 (0.10) | --- | 0.412 |
| *cis*-Nonachlor | 0.98 (0.02) | 0.92 (0.05) | 0.55 (0.04) | 15.91 (1.18) | 9.31 (3.66) | 5.41 (0.03) | 5.15 (0.16) | --- | 0.000 |
| *trans*-Nonachlor | 0.95 (0.03) | 0.94 (0.05) | 0.75 (0.00) | 28.86 (4.94) | 19.58 (7.81) | 5.67 (0.08) | 5.48 (0.16) | --- | 0.000 |
| Oxychlordane | 0.96 (0.02) | 0.97 (0.02) | 0.78 (0.32) | 29.02 (4.18) | 19.03 (10.49) | 5.67 (0.06) | 5.44 (0.22) | --- | 0.000 |
| *o*,*p*'–DDE | 0.96 (0.04) | 0.90 (0.06) | 1.60 (0.22) | 58.24 (18.07) | 27.90 (11.26) | 5.96 (0.14) | 5.63 (0.16) | --- | 0.000 |
| *p*,*p*'–DDE | 0.96 (0.03) | 0.90 (0.05) | 2.25 (0.34) | 34.08 (5.42) | 25.87 (9.71) | 5.74 (0.07) | 5.60 (0.15) | --- | 0.000 |
| *o*,*p*'–DDD | 0.98 (0.01) | 0.93 (0.05) | 0.34 (0.01) | 13.87 (1.30) | 9.69 (4.24) | 5.35 (0.04) | 5.16 (0.17) | --- | 0.000 |
| *p*,*p*'–DDD | 0.98 (0.02) | 0.94 (0.05) | 0.24 (0.01) | 9.76 (0.67) | 6.93 (2.55) | 5.20 (0.03) | 5.03 (0.14) | --- | 0.000 |
| *o*,*p*'–DDT | 0.95 (0.03) | 0.96 (0.03) | 2.11 (0.42) | 31.34 (9.50) | 30.08 (24.07) | 5.69 (0.13) | 5.57 (0.31) | --- | 0.805 |
| *p*,*p*'–DDT | 0.97 (0.03) | 0.97 (0.02) | 1.41 (0.12) | 26.72 (6.64) | 17.40 (11.16) | 5.63 (0.10) | 5.37 (0.27) | --- | 0.001 |

[a] A matrix effect term defined by Zeng and Noblet (2002) and obtained with Equation (10) from five-point linear regression.

[b] Obtained with Equation (7) with five-point linear regression.

[c] Obtained from $K_f V_f$ with a $V_f$ value of 0.612 $\mu$L.

[d] The log $K_{ow}$ values for PCB congeners are obtained from Hawker and Connell (1988), and no log $K_{ow}$ values are provided for chlorinated pesticides because existing data vary substantially.

[e] Probability that the $K_f V_f$ values for groups 1 and 2 are not significantly different ($p > 0.05$)

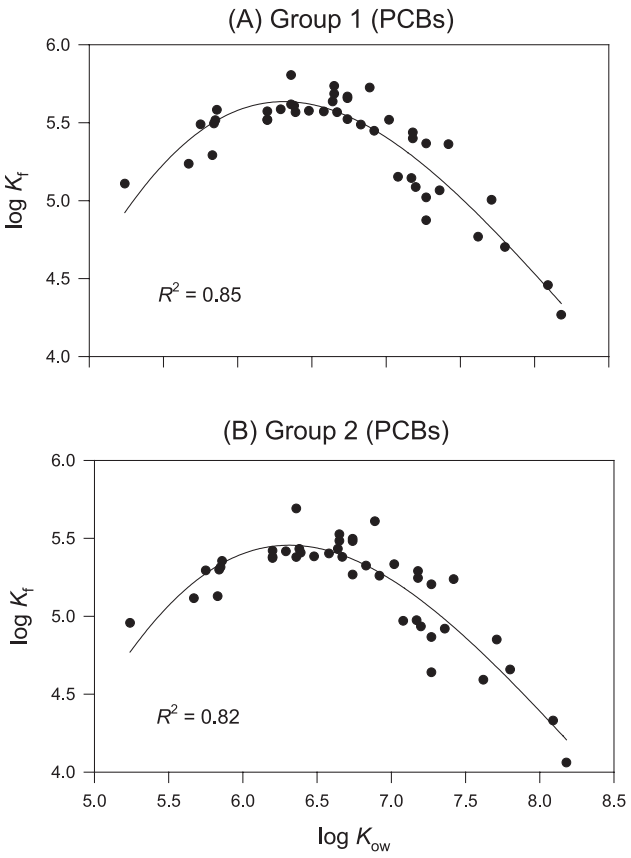


**Figure 2. Correlation of measured log Kf and log Kow for polychlorinated biphenyls (PCBs) with (A) Group 1 and (B) Group 2. Log Kow values were obtained from (Hawker and Connell 1988).**

ured by Paschke and Popp (2003) and Poreschmann *et al.* (2000) (Table 3).

The above comparison points to the significance of PDMS coating thickness to the sorption capacity for PCB congeners of different sizes. Langenfeld *et al.* (1996) also observed a substantial difference between the $K_f$ values with 7 μm and 100 μm PDMS-coated fibers for a number of PAH compounds. They attributed the difference mainly to possible different physical or chemical properties of the PDMS-coated fibers that could greatly affect the absorption of high molecular weight compounds. It is interesting to note that the correlation between log-based bioconcentration factors (BCFs) of PCBs obtained from field measurements of 10 perch individuals and log $K_{ow}$ was also a bell-shaped curve (Bremle *et al.* 1995) similar to those displayed in Figure 2. The authors ascribed it to a number of factors. Notably, solubility, fat quality, uptake rate, and hydrophobicity were considered possible factors responsible for the bell-shaped curve. Parallel to these observations, the size of PCB congeners may also play a significant role in elucidating the sorption mechanism for PDMS coatings. As the number of chlorines on the phenyl rings increases, the PCB congeners become bulky, with high electron density from the chlorines. The bulky molecules have the tendency to induce dispersive forces, which are instantaneous and repulsive in nature, from interacting with, or permeating into the PDMS phase. If the sorbent phase is also thick, the induced dispersive forces may be sufficient to substantially lower the sorption capacity for large-size PCB congeners. Obviously, more research is needed to verify this hypothesis.

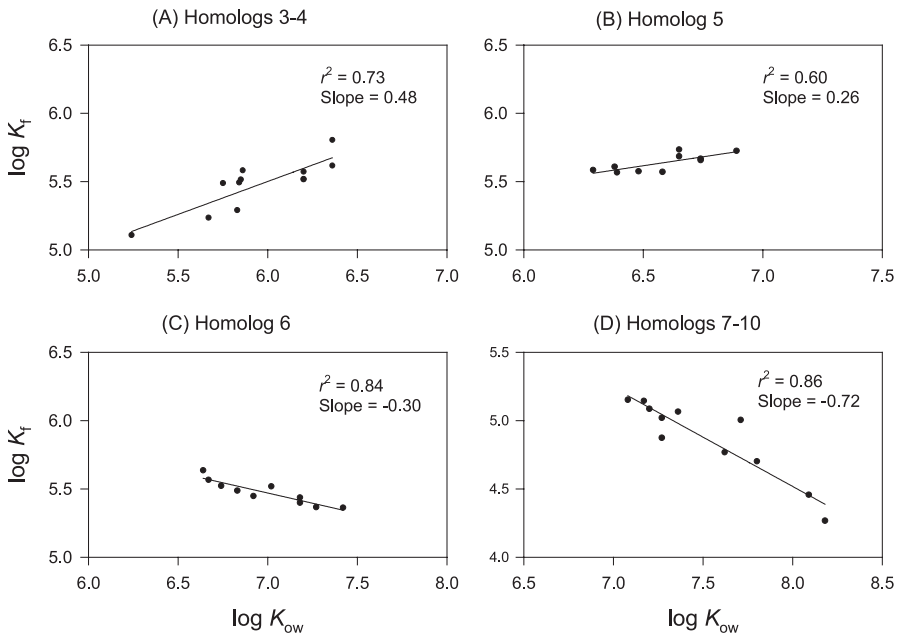


**Figure 3. Correlation of measured log $K_f$ and log Kow for polychlorinated biphenyls (PCBs) organized according to the number of chlorines (homolog): (A) homologs 3-4; (B) homolog 5; (C) homolog 6; and (D) homologs 7-10.**

## Absorption versus Adsorption

The issue of whether the SPME process with PDMS coating is absorption or adsorption has drawn heated debate (Yang *et al.* 1998, Yang *et al.* 1998, Hawthorne *et al.* 2000, Poerschmann *et al.* 2000, Vaes *et al.* 2000).

**Table 3. Comparison of experimentally measured log $K_f$ (PDMS phase-water distribution coefficient) values. All data were acquired with static SPME methods except for those by Poreschmann et al. (2000) as indicated.**

| | | log $K_f$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Present Study[a] | Mayer *et al.*[b] | | Poreschmann *et al.*[c] | | | Yang *et al.*[d] | | Paschke and Popp[e] | |
| | | (100 µm, 12d) | (15 µm, 3d) | (15 µm, 6 wk) | (7 µm, 24h) | | (7 µm, >72h) | (7 µm, 5h) | (100 µm, 24h) | (7 µm, 3d) | (100 µm, 3d) |
| Analyte | log $K_{ow}$[f] | | | | Static 1 | Static 2 | Dynamic | | | | |
| PCB 18 | 5.24 | 5.11 (0.06) | | | | | | 4.51 | 4.03 | | |
| PCB 28 | 5.67 | 5.24 (0.07) | | | 4.71 | 4.94 | 5.04 | 4.55 | 3.88 | 4.65 | 4.76 |
| PCB 44 | 5.75 | 5.49 (0.06) | | | | | | 4.75 | 3.80 | | |
| PCB 52 | 5.84 | 5.49 (0.06) | 5.30 (0.07) | 5.38 (0.11) | 4.48 | 5.21 | 5.55 | 4.67 | 3.87 | 4.98 | 5.14 |
| PCB 66 | 6.20 | 5.57 (0.06) | | | | | | 4.85 | 3.88 | | |
| PCB 77 | 6.36 | 5.80 (0.04) | | | | | | 4.92 | 3.83 | | |
| PCB 101 | 6.38 | 5.61 (0.07) | 5.58 (0.11) | 5.71 (0.06) | | | | 4.56 | 3.56 | 5.48 | 5.48 |
| PCB 105 | 6.65 | 5.73 (0.06) | 5.69 (0.02) | 5.89 (0.03) | | | | 3.56 | 3.42 | | |
| PCB 118 | 6.74 | 5.67 (0.05) | 5.69 (0.06) | 5.87 (0.03) | 4.42 | 5.52 | 5.97 | 4.56 | 3.56 | | |
| PCB 126 | 6.89 | 5.73 (0.06) | | | | | | 4.52 | 3.22 | | |
| PCB 128 | 6.74 | 5.52 (0.10) | | | | | | 4.26 | 2.88 | | |
| PCB 138 | 6.83 | 5.49 (0.09) | 5.79 (0.07) | 6.20 (0.07) | | | | 4.49 | 3.37 | 5.98 | 5.65 |
| PCB 153/168 | 6.92 | 5.45 (0.10) | 5.84 (0.08) | 6.16 (0.09) | 4.41 | 5.63 | 6.05 | 4.57 | 3.42 | 6.01 | 5.67 |
| PCB 156 | 7.18 | 5.44 (0.09) | 5.79 (0.07) | 6.28 (0.06) | | | | 4.21 | 2.92 | | |
| PCB 170 | 7.27 | 5.02 (0.13) | | | | | | 4.23 | 2.96 | | |
| PCB 180 | 7.36 | 5.07 (0.11) | 5.85 (0.06) | 6.40 (0.10) | 4.19 | 5.60 | 6.23 | 4.21 | 2.92 | 6.37 | 5.55 |
| PCB 187 | 7.17 | 5.14 (0.12) | | | | | | 4.38 | 3.26 | | |
| PCB 201 | 7.62 | 4.77 (0.12) | | | | | | 4.23 | 3.08 | | |
| PCB 206 | 8.09 | 4.46 (0.17) | | | | | | 3.79 | 2.45 | | |
| PCB 209 | 8.18 | 4.27 (0.20) | | | | | | 3.75 | 2.43 | | |
| *p,p'*–DDE | --- | 5.74 (0.07) | 5.73 (0.09) | 5.88 (0.05) | | | | | | 5.39 | 5.26 |
| *p,p'*–DDD | --- | 5.20 (0.03) | | | | | | | | 4.45 | 4.55 |
| *p,p'*–DDT | --- | 5.63 (0.10) | | | | | 5.33[g] | | | | |

[a]Extracted from the Group 1 data in Table 2.
[b]Extracted from Mayer *et al.* (2000); water volume was 1 L with an initial concentration of 100 ng/L.
[c]Extracted from Poreschmann *et al.* (2000); initial concentration of 50 ng/L and 4 mL sample volume were employed for static 1 and initial concentration of 500 ng/L and a 250 mL sample volume for static 2 employed; constant analyte concentrations were maintained during the dynamic experiments.
[d]Extracted from Yang *et al.* (1998); sample volume was 2 mL and initial analyte concentration was 50 ng/L.
[e]Extracted from Paschke and Popp (2003).
[f]Obtained from Hawker and Connell (1988).
[g] Only DDT was indicated in the paper.

Absorption is defined as a sorption process dominated by linear partitioning of the analyte into the sorbent phase; therefore, the amount of the analyte sorbed on the sorbent phase is proportional to the sorbent volume. Consequently, a linear relationship such as those shown in Figures 3a and 3b exists between log $K_f$ and log $K_{ow}$. On the other hand, adsorption is defined as a sorption process dictated by the interaction between the sorbent surface and the analyte. The amount of the analyte sorbed on the sorbent phase is proportional to the sorbent surface area instead of volume. A negative linear correlation exists between log $K_f$ and log $K_{ow}$ such as those shown in Figures 3c and 3d.

If the above arguments hold, sorption of PCBs on 7 µm and 15 µm PDMS coatings is an absorption process, whereas that of PCBs on 100 µm PDMS coating seems to be consistent with a combined process of absorption and adsorption (Table 3). Furthermore, sorption of PCB congeners on the 100 µm PDMS coating appears to proceed via absorption for PCBs in homologs 3-5 and via adsorption for PCBs in homologs 6-10 (Figure 3). However, such a description seems over-simplified. It is particularly challenged by the hypothesis of induced dispersive forces discussed in the previous section. Investigations into the structure of PDMS coating and the interacting forces between PCBs and the PDMS phase are necessary to better understand the mechanism of SPME processes.

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