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Journal of Chromatography A, 1116 (2006) 240–247
JOURNAL OF CHROMATOGRAPHY A
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Application of a static solid-phase microextraction procedure combined with liquid–liquid extraction to determine poly(dimethyl)siloxane–water partition coefficients for selected polychlorinated biphenyls

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Received 10 January 2006; received in revised form 8 March 2006; accepted 9 March 2006
Available online 31 March 2006

Abstract

A static solid-phase microextraction (SPME) procedure combined with liquid–liquid extraction (LLE) was used to determine the poly(dimethyl)siloxane (PDMS)–water partition coefficients (K_f) for selected polychlorinated biphenyl congeners (PCBs), including PCB 1, 15, 28, 47, 101, 153, 180, 202, 206, and 209. The accuracy for the measurements of analyte concentrations in the aqueous phase was ensured with a one-to-one recovery correction strategy employing one ^{13}C-labeled PCB congener as a surrogate standard for each unlabeled PCB counterpart. The effects of coating thickness (7, 30, and 100 μm) and sample volume (130 mL and 2 L) on the K_f values were examined experimentally and confirmed with paired *t*-tests. Significant dependence of K_f values on coating thickness was found for a few heavily chlorinated congeners only, and was tentatively attributed to the use of the inaccurate effective coating volumes and the structural variation with these PDMS coatings. In addition, no significant differences in the log K_f values of all analytes except for PCB 206 were found between the sample sizes of 130 mL and 2 L for both the 7- and 100-μm coatings. Overall, K_f values obtained with 2-L sample containers were consistently higher than those reported in the literature, which is attributable to the selection of appropriate equilibrium times for SPME and direct measurements of aqueous analyte concentrations with LLE in the present study.

Keywords: Solid-phase microextraction; Partition coefficient; Very hydrophobic organic compound; Liquid–liquid extraction; One-to-one recovery correction

1. Introduction

Partition coefficients of very hydrophobic organic chemicals (VHOCs) between an "aploar" and a "polar" phase are of importance because concentrations of residual VHOCs in the atmosphere, water, and soil and their bioavailability strongly depend on partition properties [1,2]. Solid-phase microextraction (SPME), as a simple, efficient, and solventless sample preparation method, has been applied to the determination of partition coefficients for various environmental media. The key to such applications is to calibrate the coefficients (K_f) of partitioning between the polymer-coated fiber and the aqueous phase for the analytes of interest. Values of K_f have been measured for a large number of organic compounds [3–12].

Two main experimental procedures have been used for determining K_f values of VHOCs, i.e., dynamic [8,9] and static methods [7,10–12]. The dynamic approach employs a dynamic source that continuously supplies the analytes of interest to the SPME system to offset any possible losses of the analytes due to SPME depletion, sorption to the container surfaces, partial precipitation, or poor dissolution. Poerschmann et al. [8] designed a generator column to determine K_f values for a series of polychlorinated biphenyls (PCBs) (from PCB 1 to PCB 180), polycyclic aromatic hydrocarbons (PAHs) (from naphthalene to benzo[*a*]pyrene), and *n*-alkanes (from *n*-octane with to *n*-tetradecane); this system is a solvent-free approach. Shurmer and Pawliszyn [9] investigated a flow-through system to test a series of PAHs from naphthalene to benzo[*a*]pyrene. Despite the appar-

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doi:10.1016/j.chroma.2006.03.029

ent advantages of the dynamic approach, the experimental setup of a typical dynamic method is generally cumbersome. Static SPME procedures used in a closed system where single- [10,11] and multi-point [7] calibration strategies were employed have also been exploited. The apparent drawbacks with this approach are the possible occurrence of large measurement errors if the analyte amount (N_f) in the sorbent phase is approaching the initial analyte amount (N_0) and adsorption of VHOCs by system surfaces (N_b term) is not accounted for. A previous study suggested that adsorption to system surfaces were not negligible even after the glassware was deactivated by appropriate procedures [13].

More recently, Ter Laak et al. [14] developed a dosing technique to determine K_f values, where a poly(dimethyl)siloxane (PDMS)-coated fiber loaded with the analytes of interest in a methanol–water mixture was allowed to equilibrate with water and the depleted amounts of the analytes in the PDMS phase were monitored. By varying the volume water/volume PDMS ratio, a K_f value could be calculated from the change of the ratio of the equilibrium and initial analyte concentrations in the PDMS phase. This approach practically avoided the direct measurement of analyte concentrations in the aqueous phase, which is particularly challenging for VHOCs. However, adsorption of the target chemicals to the container surfaces during the depletion process was not quantified, which could greatly impact the results.

Given the importance of adsorption to system surfaces widely recognized by many researchers [4,5,15–19], the key to a successful determination of K_f is to measure truly dissolved concentrations in the aqueous phase. A review of the techniques for such a purpose indicates that liquid–liquid extraction (LLE) has remained the commonly used method regardless of whether a dynamic or static method is involved. Based on this assessment, the present study was initiated to develop a static extraction procedure employing LLE for a direct quantification of dissolved concentrations. Ten PCB congeners representative of mono-chlorinated to deca-chlorinated isomeric groups with a wide range of hydrophobicities, often characterized by the octanol–water partition coefficient (K_{ow}), were selected as target analytes (Table 1). To ensure the accuracy of LLE, one ^{13}C-labeled PCB congener was selected as a surrogate standard for each PCB analyte to allow one-to-one recovery correction. Three PDMS coatings, 7-, 30-, and 100-μm, were chosen to examine the effects of coating thickness on the K_f values. In addition, sample containers of 2 L and 130 mL were used to evaluate any variability of K_f caused by various sample sizes.

Table 1
The structure, log K_{ow}, and water solubility at 25 °C (S_w, ng/L) of the analytes

Name	Structure	Log K_{ow}[a]	S_w[b] (ng/L)
PCB 1	2-	4.46	3.28×10^6
PCB 15	4,4′-	5.3	1.80×10^5
PCB 28	2,4,4′-	5.67	5.79×10^4
PCB 47	2,2′,4,4′-	5.85	2.26×10^4
PCB 101	2,2′,4,5,5′-	6.38	8.20×10^3
PCB 153	2,2′,4,4′,5,5′-	6.92	1.10×10^3
PCB 202	2,2′,3,3′,5,5′,6,6′-	7.24	2.23×10^2
PCB 180	2,2′,3,4,4′,5,5′-	7.36	3.68×10^2
PCB 206	2,2′,3,3′,4,4′,5,5′,6-	8.09	35.8
PCB 209	2,2′,3,3′,4,4′,5,5′,6,6′-	8.18	10.5

[a] The log K_{ow} values of PCB congeners were obtained from the reference [28].
[b] The S_w values were abstracted from the reference [25].

2. Materials and methods

2.1. Materials

All unlabeled PCB congeners were purchased from AccuStandards (New Haven, CT, USA), and the corresponding ^{13}C-labeled counterparts were obtained from Cambridge Isotope Laboratory (Anbe, MA, USA). The structures, log K_{ow} values, and water solubility data at 25 °C (S_w) of the unlabeled PCBs are detailed in Table 1. Hexane, toluene, acetone, and dichloromethylene (DCM) of pesticide residue analysis grade were supplied by Riedel-de Haën (Seelze, Germany). Double distilled water with dissolved organic carbon of 0.059 mg/L was used as spiking medium.

2.2. SPME procedures and sample preparation

SPME fibers with 7-, 30-, and 100-μm PDMS coating (Supelco, Bellefonte, PA, USA) were conditioned at 320, 250, and 250 °C under helium (of 99.999% purity) stream on a GC injection port for 1, 0.5, and 0.5 h, respectively, prior to initial use. Glass containers of ∼2 L and 130 mL were washed with detergent and tap water, rinsed with double distilled water, kilned at 450 °C for at least 4 h. Immediately prior to use, each 2-L flask was silanized with a solution of 15% dimethyldichlorosilane (Fluka, Buchs, Switzerland) in toluene for ∼3 min and allowed to dry for 1 h at ambient temperature after the rinsate was discarded. The silanization process was repeated three times. Each 130-mL container was silanized by soaking in the same solution for 24 h. All silanized containers were rinsed twice with toluene and three times with methanol, dried at 120 °C, and rinsed with double distilled water at least three times. PTFE-coated stirring bars were rinsed with double distilled water, sonicated in DCM for 10 min, and dried at 100 °C.

Custom-made mixtures of the target PCB congeners at 2000 μg/mL each in hexane:toluene (V_{hexane}:$V_{toluene}$ = 98:2) were diluted with acetone to make up 2 μg/mL spiking solutions. Each flask was filled with ∼2 L or 130 mL of double distilled water and spiked with the spiking solution of different volumes. One stirring bar was placed in the flask. An antibiotic agent, sodium azide of analytical reagent (Shanghai Chemical Reagent, Shanghai, China) at 0.2 mg/mL, was added to the flask. A silanized PTFE sheet was bound to the opening of the flask with rubber bands to seal the system. An SPME fiber was pierced through the PTFE sheet and into the spiked water after the spiking solution had been dispersed completely. The PDMS-coated fiber was protracted and exposed to the spiked water. The flask was placed on a magnetic stirrer (Jiangsu Ronghua Instrument, Jintan, China) at 800 and 600 rpm, respectively, for the 2-L and 130-mL flasks. All experiments were conducted at controlled temperatures of 25 ± 2 °C. At the end of the extraction, the

PDMS-coated fiber was removed with care from the flask and shaken vigorously and gently touched the tip of the needle with a tissue to remove any water residues before being retracted into the needle sleeve. Analytes sorbed on the SPME device were thermally desorbed into the GC injector on the GC/MS instrument described later. Possible carryover was minimized by keeping the SPME fiber in the injector for an additional 5 min after injection. Blanks were run periodically to confirm the absence of interferences. SPME fibers were generally processed on the same day when extraction was complete (all within 24 h). SPME fibers not analyzed immediately were stored at −20 °C.

2.3. Liquid–liquid extraction procedures

LLE was performed on the aqueous samples upon SPME extraction. The general procedure was similar to the method 3510C (Separatory Funnel Liquid–Liquid Extraction) recommended by the U.S. Environmental Protection Agency [20], and only a brief description is presented herein. One liter or 130 mL of water from the 2-L or 130-mL sample container upon SPME was quantitatively transferred to a 2-L or 250-mL separatory funnel. ^{13}C-labeled PCB congeners corresponding to all unlabeled PCB analytes were added to the funnel. Each sample was extracted three times, each with 100 or 13 mL of DCM. The organic layers from three extractions were combined and concentrated to ∼1–2 mL with a Zymark Turbo Vap II (Hopkinton, MA, USA) at 28 °C. The extract was passed through anhydrous sodium sulfate (analytical reagent, Riedel-de Haën) to remove residual water, the concentrator was rinsed with hexane, and the extract was solvent-exchanged to hexane. The hexane solution was collected in a 250-mL concentrator, evaporated to 0.5 mL under a gentle N_2 stream, and quantitatively transferred into a 2-mL vial. Before GC/MS analysis, the internal standards, PCB 18 and PCB 197, were added into the extract.

The recoveries of ^{13}C-labeled PCB 1, 15, 28, 47, 101, 153, 180, 202, 206, and 209 were used to correct the concentrations of their unlabeled counterparts in each LLE sample. To demonstrate the variability of the extraction method performance, the average recoveries of the ^{13}C-labeled PCB congeners were calculated for a total of 75 samples, which were 58.4 ± 11.6%, 64.1 ± 9.5%, 63.7 ± 10.9%, 67.6 ± 11.7%, 72.1 ± 12.7%, 80.4 ± 11.5%, 83.0 ± 10.2%, 104.4 ± 11.6%, 106.9 ± 16.3%, and 97.4 ± 11.1%, respectively.

2.4. GC/MS analysis

Analyses were carried out with a Varian Saturn 2200 GC/ion trap-MS system (Walnut Creek, CA, USA), equipped with a 1079 split/splitless injector and an 8410 auotsampler. A 60 m × 0.25 mm i.d. with a 0.25 μm film thickness DB-5 column was used for chromatographic separation. The column temperature was programmed from 100 °C (held for 1 min) to 220 °C at a rate of 8 °C/min, and further increased at a rate of 10 °C/min to 290 °C where the temperature was held for 10 min. Ultrahigh purity helium was employed as carrier gas at a constant flow of 1.3 mL/min. Injector temperature was held constant at 280 °C. Mass spectra were acquired in the positive electron impact mode at 70 eV by the full scan and selective ion storage (SIS) methods, respectively, for SPME fibers and LLE samples. The temperatures of the ion trap, manifold, and transfer line temperature were maintained at 190, 40, and 280 °C, respectively. The retention times and SIS ranges for the target analytes and the quantification ion ranges for both the labeled and unlabeled PCBs are listed in Table 2.

Table 2
Retention times (R_t), selective ion storage (SIS) ranges, and quantification ion ranges for the target analytes

Compound	R_t (min)	SIS range (*m/z*)	Quantification ion range (*m/z*)	
			Unlabeled	^{13}C-labeled
PCB 1	13.1	184–208	188–190	200–202
PCB 15	17.2	218–246	222–224	234–236
PCB 28	18.7	254–272	256–258	268–270
PCB 47	20.2	286–312	290–294	302–306
PCB101	23.8	322–346	324–328	336–340
PCB 153	28.5	356–382	358–362	370–374
PCB 202	33.0	390–450	426–432	438–444
PCB 180	34.2	390–438	392–398	404–410
PCB 206	41.2	458–482	460–466	472–478
PCB 209	43.2	492–522	496–502	508–514
PCB 18[a]	17.0	254–262	256–258	
PCB 197[a]	34.0	394–404	428–432	

[a] Used as internal standards.

2.5. Quantification of MS responses

Prior to analysis of each SPME fiber, 1 μL of the standard mixture containing all analytes at 20 μg/mL each 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 fibers were used to calculate the analyte amounts. Standard solutions containing various concentrations of the target analytes (0.5, 2, 10, 20, 50, and 100 μg/mL) and internal standards were prepared in hexane solvent to create calibration curves. The linear correlation coefficient (r^2) for all analytes were better than 0.99 within the range of 0.5–100 μg/mL, allowing the use of single-point external calibration method in this range with accuracy.

An internal calibration method was used to determine analyte concentrations in the LLE samples. Mixtures of the unlabeled and ^{13}C-labeled PCBs at 5, 10, 20, 50, 100, 200, and 500 ng/mL and internal standards PCB 18 and 197 at 200 ng/mL were prepared in hexane, and 1 μL of each of these mixtures was injected into the GC/MS instrument with the Varian 8410 autosampler to generate calibration curves for quantification.

2.6. Kinetic experiments

Time-series experiments were conducted in 130-mL flasks with 7-, 30-, and 100-μm coatings and a spiking concentration of 1 ng/mL for all analytes. Sample processing timepoints were selected at 1, 2, 4, 8, 12, 16, 20 and 30 days, respectively, and triplicate samples were processed at each timepoint. Time to equilibrium was determined for each analyte from the ratio of concentrations in the PDMS coating and the aqueous phase. In

addition to this complete kinetic profiling, 2-L flasks were also used to conduct 24- and 40-day extractions at 0.1 ng/mL for all analytes to estimate the times to equilibrium for the 7- and 100-μm coatings.

2.7. Determination of K_f values

Spiked water samples contained in 2-L and 130-mL flasks were prepared with each analyte at 0.1 and 1 ng/mL, respectively. Extraction times were 12, 16, and 20 days in 130-mL sample and 24, 40, and 40 days in 2-L sample for 7-, 30-, and 100-μm PDMS coatings, respectively. The absolute analyte amount (N_f^∞) extracted by the SPME fiber were calculated from the external calibration response factors obtained from syringe injection of a standard solution containing all analytes at 20 μg/mL in hexane. The concentrations of the analytes in the aqueous phase (C_w^∞) after SPME were determined from the internal calibration method as described above. K_f can be expressed as

$$K_f = \frac{C_f^\infty}{C_w^\infty} = \frac{N_f^\infty}{V_f C_w^\infty}$$

where V_f is the volume of the PDMS coating. Each reported K_f value was an average of three measurements. Paired *t*-test was conducted using Microsoft Excel to examine if there was significant different ($p < 0.05$) between two sets of K_f values acquired with different coatings or sample sizes for a given analyte.

To examine whether there was any interference with the SPME procedures, blank experiments were performed with 130-mL flasks for each coating thickness (adding the same solvent to 130-mL flasks without analytes). Analyses of the PDMS fibers and aqueous samples found no detectable amounts of any analytes.

3. Results and discussion

3.1. Selection of PCB congener concentrations

The analyte concentrations in the aqueous phase after SPME are dictated by the initial spiking concentrations, water solubility of the analytes, instrument detection capability, and sample size. To estimate the spiking analyte concentrations needed for an accurate determination of the analyte concentrations in the aqueous phase, spiking samples at 0.01, 0.1, and 1 ng/mL for each analyte in 130-mL flasks were subject to LLE after SPME. The results indicated that the analytes in the aqueous phase were hardly detectable with the 0.01 and 0.1 ng/mL spiked samples, especially for several heavily chlorinated PCB congeners, whereas they were satisfactorily abundant in the 1 ng/mL sample for GC/MS analysis. Therefore, the concentration of 1 ng/mL for all analytes was used with 130-mL flasks in all other experiments. Similarly, the concentrations of all analytes were selected at 0.1 ng/mL when 2-L flasks were used. It should be noted that although the spiking concentrations of several PCB congeners were higher than their S_w, higher measured water concentrations (C_w^∞) than S_w occurred for PCB 206 and 209 only with the 130-mL sample size (details to be discussed later). In addition, measured C_w^∞ values were lower than S_w for all the target analytes with the 2-L sample size.

The unlabeled and ^{13}C-labeled polybrominated biphenyl ether and PCB congener pairs coelute chromatographically [21,22], and hexa- to deca-cholrinated or brominated pairs even possess partially overlapping ion fragment profiles. Our previous study [23] indicated that only the quantitation of ^{13}C-labeled PCBs was interfered by the presence of unlabeled counterparts, because the quantitation ions for unlabeled PCB congeners can be so chosen as to steer clear of any contribution from the ^{13}C-labeled counterparts (Table 2). Furthermore, the magnitude of these interferences can be estimated by theoretical predictions so that the proper range of the concentration ratios of ^{13}C-labeled and unlabeled counterparts can be selected to satisfy a preset quantitation error. In the present study, the concentrations of the ^{13}C-labeled PCB congeners were all 26 ng/mL in LLE experiments and the LLE recoveries for hexa- to deca-CB congeners (PCB 153 to PCB 209 in Table 1) were in the range of 80–107%. If we assume the LLE recovery is 100% for all the unlabeled PCBs and when the quantitation ion range are selected as shown in Table 2, the concentrations of unlabeled PCB 153, 180, 202, 206, and 209 should be less than 5233, 1050, 317, 127, and 70 ng/mL, respectively, in order to maintain a quantitation error less than 5% for ^{13}C-labeled PCBs according to theoretical predictions [23]. In this study, the actual concentrations of unlabeled PCB congeners were always lower than the values mentioned above. Therefore, the interferences to the quantitation of ^{13}C-labeled PCBs from the presence of unlabeled PCBs could be neglected.

3.2. Determination of time to equilibrium

Fig. 1 illustrates the variability of the ratio C_f/C_w (designated as K), where C_f and C_w are analyte concentrations in the PDMS phase and water, respectively, at any timepoint, with time for 7-, 30-, and 100-μm PDMS-coated fibers in the 130-mL sample containers. The time to equilibrium increased with increasing molecular weights and coating thickness. For the 7-μm coating, K values became constant after 2–5 days of extraction for PCB 1 to PCB 101, 8 days for PCB 153, and 12 days for PCB 180, 202, 206, and 209. For the 30-μm coating, K values reached constant after 4 days for PCB 1 to PCB 47, 12 days for PCB 101 to 153, and 16 days for PCB 180 to PCB 209. For the 100-μm coating, K values reached constant after about 1–2 days for PCB 1 to PCB 28, 8 days for PCB 47, 12 days for PCB 101, and about 20 days for PCB 153 to PCB 209. As a result, 12, 16, and 20 days were selected as the times to equilibrium for the 7-, 30-, and 100-μm PDMS coatings, respectively.

Comparison of the K values at 24 and 40 days was also conducted with 2-L flasks for the 7- and 100-μm coatings. For the 7-μm coating, there was no significant difference in log K values between 24 and 40 days for all analytes. In addition, no significant difference in log K values was found between 20 and 40 days for all congeners except for PCB 153 with the 100-μm coating. Therefore, 24 and 40 days were selected as the times to equilibrium for determination of K_f values with 7- and 100-μm

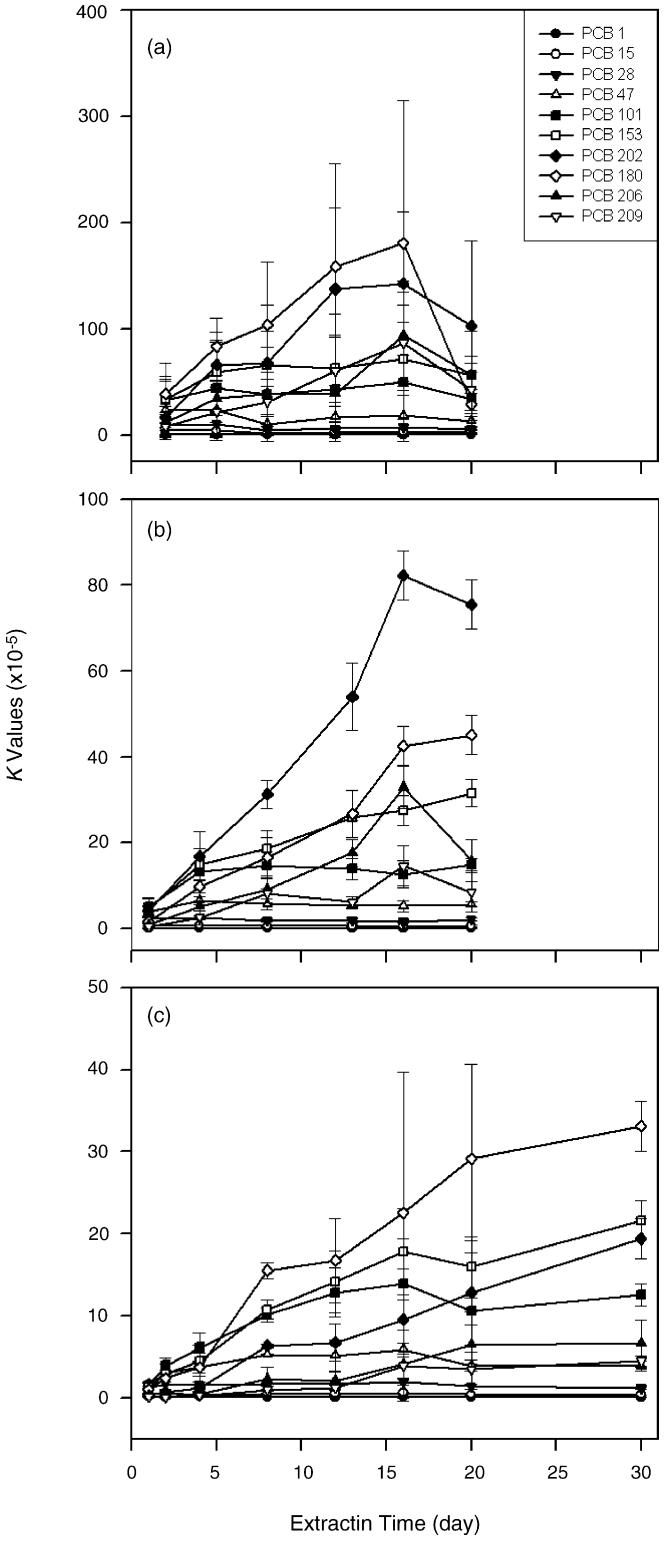

Fig. 1. Kinetic profiles of PCB congeners, expressed as the C_f/C_w ratio (K) vs. extraction time, prepared at 1 ng/mL in 130-mL flasks for different PDMS coatings: (a) 7 μm; (b) 30 μm; and (c) 100 μm.

coatings, respectively, in 2-L flasks. The reason for the significant difference in log K values for PCB 153 with the 100-μm coating remains unknown, and is probably attributable to experimental artifacts.

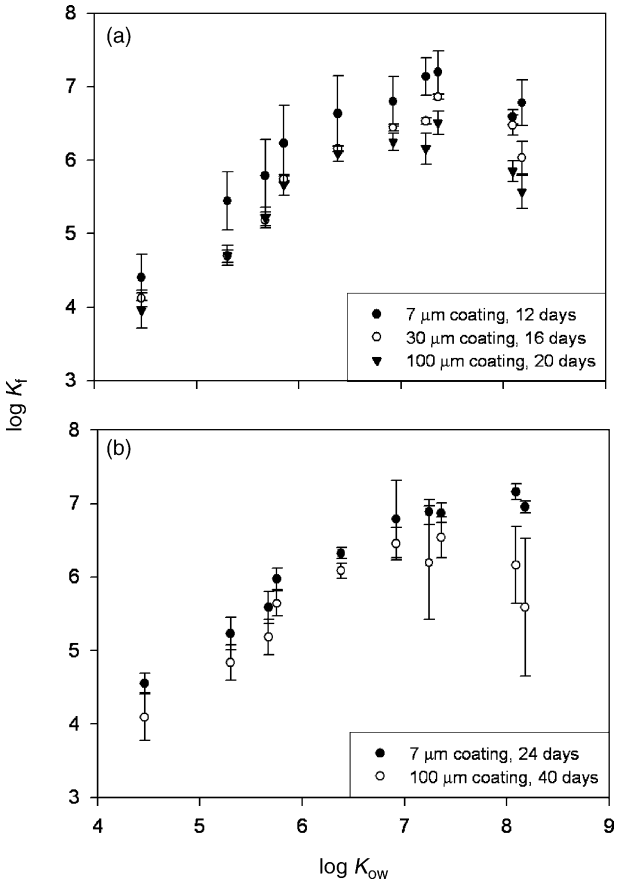

Fig. 2. Relationship between log K_f and log K_{ow} for different PDMS coatings: (a) 130-mL sample size with 1 ng/mL concentration and (b) 2-L sample size with 0.1 ng/mL concentration.

3.3. Effects of coating thickness on K_f values

The log K_f values qualitatively show the following order for all analytes: 7 μm > 30 μm > 100 μm (Fig. 2). In addition, the K_f values with the 7-μm coating endured larger errors than those with the 30- and 100-μm coatings in most cases (Figs. 2 and 3), probably attributable to the lower sorption capacity of the 7-μm coating that caused a higher deviation in measured amounts of the analytes sorbed. However, paired t-tests indicated no significant difference in log K_f values between different PDMS coatings for most of the analytes ($p > 0.05$; Table 3). Significant difference in log K_f was detected only for PCB 206 between the 30- and 100-μm coatings with the 130-mL flask, for PCB 180, 202, 206, and 209 between the 7- and 100-μm coatings with the 130-mL container, and for PCB 206 and 209 between the 7- and 100-μm coatings with the 2-L sample size ($p < 0.05$; Table 3). The dependence of K_f values on the PDMS coating thickness was reported for several PAHs [24] and heavily chlorinated PCB congeners [10], most notably for the high molecular weight compounds. However, no statistical test was carried out to examine if this dependence was significant in the previous studies. Furthermore, the sorption to the container walls was not accounted for in the previous results, whereas the present study employed the LLE method to directly determine the true aqueous concentrations of the analytes after SPME.

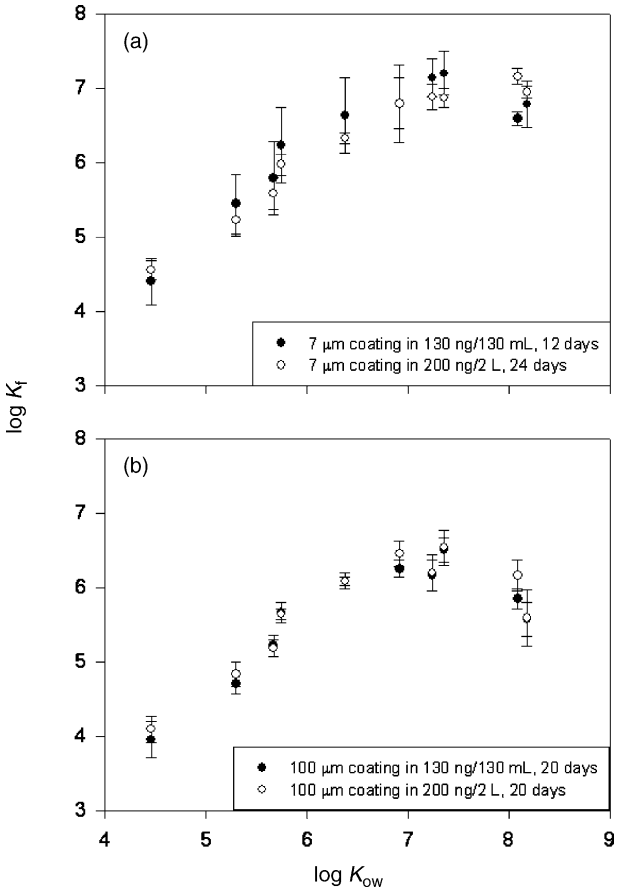

Fig. 3. Relationship between log K_f and log K_{ow} for the 7- and 100-μm PDMS coatings with different sample sizes: (a) 7-μm coating in 130-mL and 2-L flasks with initial concentrations of 1 and 0.1 ng/mL, respectively, and (b) 100-μm coating in 130-mL and 2-L flasks with initial concentrations of 1 and 0.1 ng/mL, respectively.

Seemingly, K_f values would be identical for a given analyte regardless of the coating thickness. Several explanations have been given to account for the observed difference in log K_f values for different coatings. The first explanation was that the extraction with the 100-μm coating did not reach the equilibrium state. This is unlikely a valid explanation in the present study, because K_f values obtained with an extraction time of 30 days were essentially the same as those with 20 days on with the 100-μm coating. The second explanation is possibly the use of incorrect coating volumes for different thicknesses. The V_f values used in this study were obtained from a previous study [9]. Langenfeld et al. [24] attributed this phenomenon to one of the two possibilities: either the true coating volumes of the 30- and 100-μm coatings were significantly less than the reported values, or the 7-μm coating might allow more adsorption to active sites on the fused silica rod, resulting in higher K_f values relative to the 30- and 100-μm coatings. The third explanation is the structural difference between the 7-μm coating and the 30- and 100-μm coatings. According to the manufacturer, Supelco, polymer particles used in the commercially available 7-μm PDMS coating are "bonded" to the silica core, whereas those in the 30- and 100-μm coatings are considered "nonbonded". This difference may have resulted in substantial differences in the apparent sorption capacities of the different coatings than what the reported coating volumes indicate.

Table 3
p-values from *t*-test of log K_f values for PCB congeners with different coatings

Analyte	130 mL[a]			2 L[b]
	7 and 30 μm	30 and 100 μm	7 and 100 μm	7 and 100 μm
PCB 1	0.233	0.420	0.114	0.109
PCB 15	0.186	0.927	0.116	0.339
PCB 28	0.221	0.776	0.293	0.263
PCB 47	0.237	0.488	0.325	0.214
PCB 101	0.237	0.472	0.381	0.229
PCB 153	0.244	0.114	0.125	0.527
PCB 202	0.224	0.119	**0.010**	0.136
PCB 180	0.250	0.066	**0.027**	0.313
PCB 206	0.265	**0.011**	**0.003**	**0.031**
PCB 209	0.213	0.096	**0.002**	**0.033**

Bold numbers indicate that the difference was significant ($p < 0.05$).
[a] A spiking concentration at 1 ng/mL for each congener.
[b] A spiking concentration at 0.1 ng/mL for each congener.

3.4. Effects of sample volume on K_f values

Two sample volumes, 130 mL and 2 L, were used with the 7- and 100-μm coatings to examine the effects of sample volume on K_f values, and the results are displayed in Fig. 3. The log K_f values for the 7-μm coating with the 130-mL sample volume were slightly higher than those with the 2-L samples for PCB 1 to PCB 180, and slightly lower for PCB 206 and 209 with the 130-mL volume than with the 2-L volume (Fig. 3(a)). On the other hand, the measurement variability with the 100-μm coating (Fig. 3(b)) appeared to be smaller than that with the 7-μm coating (Fig. 3(a)). Paired *t*-test results indicate that significant differences in log K_f values between the two sample volumes were found only for PCB 206 with both the 7-μm ($p = 0.044$) and 100-μm ($p = 0.027$) coatings. As a result, it can be concluded that K_f values are independent of sample size used for the experiments.

It should be noted that measured K_f's for PCB 206 and PCB 209 with the 130-mL flasks could carry large uncertainties because the solubilities (Table 1) of these two compounds were lower than their measured aqueous concentrations (C_w^∞) after SPME. The measured C_w^∞ of PCB 206 and 209 in the 130-mL samples were 105.7 ± 5.3 ng/L and 49.4 ± 11.6 ng/L for the 7-μm coating, and 48.1 ± 6.2 ng/L and 32.7 ± 8.5 ng/L for the 100-μm coating, compared with their respective solubilities of 35.8 and 10.5 ng/L [25]. Although adsorption to the container surfaces and absorption to the PDMS coating may have depleted a large portion of VHOCs in the 130-mL samples, microdroplets or microcrystals of insoluble analytes could still form in the aqueous phase, especially for PCB 206 and 209, because of the high analyte concentrations in the system. To minimize any errors stemming from this source, a calibration procedure can be adopted. When the measured C_w^∞ of a chemical is higher than its solubility, the SPME process can be regarded as a non-depletive extraction such that the extracted fraction in the aqueous phase can be refilled by release of the chemical from microdroplets or

microcrystals [26,27]. In this regard, the truly dissolved concentration of the chemical can be replaced with its S_w. The corrected K_f value (K_f^c) can be expressed as $K_f^c = C_f^\infty / S_w$.

Overall, the 2-L sample size appears to be equivalent to or superior over the 130-mL size in measuring K_f. At least the 2-L sample size allows the measurement of the analyte aqueous concentrations at levels below the analyte solubilities. In the following section, only the K_f values obtained with the 2-L flasks will be used to compare with those from previous studies.

3.5. Comparison with previous studies

A number of studies obtained K_f values for selected PCB congeners with PDMS-coated fibers (Table 4). Apparently, a large variability in K_f values has been obtained with different experimental procedures, PDMS coating thicknesses, and research groups. For example, the lowest K_f values were obtained by Yang et al. [5], who used a static SPME method to determine K_f values on 7- and 100-μm PDMS-coated fibers in 2-mL sample size. Mayer et al. [7] obtained higher K_f values with increasing K_{ow} values with 6-week extraction compared to 3-day extraction using a 15-μm coating. Sufficient equilibrium time was cited as an important factor to achieve appropriate K_f values. Poershcmann et al. [8] acquired higher K_f values with a larger sample volume (250 mL) than with a smaller one (4 mL) using a static procedure. They were able to achieve even higher K_f values using a dynamic method. Paschke and Popp [10] used a static method to determine K_f values on 7- and 100-μm PDMS-coated fibers in an Erlenmeyer flask (with a sample size of 480 mL). More recently, Zeng et al. [12] cleaned glassware using solvent to determine the sorbed amounts of analytes by glass container when no SPME fibers inserted into samples, and then calculated C_w^∞ by deducting the amounts of analytes sorbed on glass container surfaces and the amounts by PDMS coatings from the initial added amounts of analytes and determined K_f values on 100-μm PDMS-coated fibers.

The K_f values obtained in the present study with the 7- and 100-μm coatings and 2-L flasks were consistently higher than those reported in the literature (Table 4). In all previous static methods, the measured C_f^∞ appeared to be accurate when equilibrium extraction was fulfilled. However, the accuracy for the measurement or estimation of C_w^∞ seemed doubtful, as C_w^∞ was not measured directly in these studies. Losses of analytes due to adsorption to system surfaces, which was neglected by most static methods, would incur an overestimation of C_w^∞ and consequently an underestimation of K_f. Adsorption to system surfaces would also amplify the dependence of K_f values on sample size, because a smaller container has a larger surface area to volume ratio than a larger one, exaggerating the effects of surface adsorption. Among all of the previous measurements, the K_f values of PCB congeners acquired through a dynamic method [8] combined with LLE to measure C_w^∞ directly are the highest. However, insufficient extraction time (96 h) or a slow analyte redelivery by a generator column may have underestimated C_f^∞, resulting in the K_f values lower than those from the present study. The authors also reported dependence of absolute K_f values on coating thickness [8], but paired *t*-tests conducted

Table 4
Comparison of log K_f values determined from the present and other previous studies

Analyte	Log K_{ow}[a]	Present study[b]		Mayer et al.[c]		Porschmann et al.[d]			Paschke and Popp[e]		Zeng et al.[f]	Yang et al.[g]	
		7 μm/24 d	100 μm/40 d	15 μm/3 d	15 μm/42 d	7 μm/24 h static 1	7 μm/24 h static 2	7 μm/96 h dynamic	7 μm/3 d	100 μm/3 d	100 μm/12 d	7 μm/5 h	100 μm/24 h
PCB 1	4.46	4.44 (0.13)	4.09 (0.18)			4.45	4.01	4.03					
PCB 15	5.3	5.11 (0.22)	4.83 (0.17)			4.55	4.63	4.65					
PCB 28	5.67	5.47 (0.21)	5.18 (0.11)			4.71	4.94	5.04	4.65	4.76	5.24 (0.07)	4.55	3.88
PCB 47	5.85	5.86 (0.14)	5.64 (0.07)										
PCB 101	6.38	6.21 (0.08)	6.08 (0.05)	5.58 (0.11)	5.71 (0.06)				5.48	5.48	5.61 (0.07)	4.56	3.56
PCB 153	6.76	6.68 (0.52)	6.45 (0.17)	5.84 (0.08)	6.16 (0.09)	4.41	5.63	6.05	6.01	5.67	5.45 (0.10)	4.57	3.42
PCB 202	7.24	6.77 (0.17)	6.20 (0.24)										
PCB 180	7.36	6.76 (0.13)	6.54 (0.23)	5.85 (0.06)	6.40 (0.10)	4.19	5.60	6.24	6.37	5.55	5.07 (0.11)	4.21	2.92
PCB 206	8.09	7.04 (0.11)	6.16 (0.21)								4.46 (0.17)	3.79	2.45
PCB 209	8.18	6.84 (0.08)	5.59 (0.38)								4.27 (0.10)	3.75	2.43

[a] The log K_{ow} data were obtained from reference [28].
[b] All data were acquired using 2-L flasks with a spiking individual concentration of 100 ng/L for all analytes.
[c] Extracted from the reference [7]. Sample sizes were 90 and 900 mL with a spiking concentration at 100 ng/L.
[d] Extracted from the reference [8]. Static 1 used 4-mL sample volume with a spiking analyte concentration of 50 ng/L, static 2 used 250-mL sample volume with an initial concentration of 500 ng/L, and the dynamic method maintained constant analyte concentrations during extraction.
[e] Extracted from the reference [10]. Sample size was 480 mL with a spiking individual concentration of 100–200 ng/L.
[f] Extracted from the reference [12]. Sample size was 1.6 L with spiking analyte concentrations of 50 ng/L.
[g] Extracted from the reference [5]. Sample size was 2 mL with a spiking analyte concentration of 50 ng/L.

in the present study suggested that the visual difference in K_f values between different coating thicknesses was only moderately significant. Evidently, sorption of VHOCs to the PDMS phase depends on the effective coating volume but not the coating surface area. Overall, the highest measured K_f values acquired in the present study compared to other previous results (Table 4) are reasonable and probably attributable to the selection of sufficient times to equilibrium and the accurate LLE measurements of C_w^∞ combined with one-to-one recovery correction. These K_f values can be used in future research to measure the concentrations of the selected PCB congeners using an SPME-based quantitation method.

Finally, the relationships between $\log K_f$ and $\log K_{ow}$ have been often used to judge whether the underlined SPME process was via absorption (linear) or adsorption (nonlinear) [8]. The results from the present study (Figs. 2 and 3) appear to support the adsorption theory for SPME of PCB congeners with the PDMS coating; however, the situation may not be as straightforward as the results seemingly suggest. Additional investigations into this issue are necessary before any definite conclusion can be drawn.

Acknowledgements

This study was financed by the "One Hundred Talents" Program of the Chinese Academy of Sciences, the National Natural Science Foundation of China (No. 40532013), and the Cooperative Institute for Coastal and Estuarine Environmental Technology (USA) (Contract No. NA05NOS4191149).

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