

Determination of poly(dimethyl)siloxane–water partition coefficients for selected hydrophobic organic chemicals using ^{14}C -labeled analogs

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Abstract

Aqueous solutions of ^{14}C -labeled analogs of seven hydrophobic organic chemicals (HOCs) were subject to solid-phase microextraction (SPME) under static conditions to assess their multi-compartment distribution and to compare poly(dimethyl)siloxane (PDMS)–water partition coefficients (K_f values) with previously reported values. To accomplish this, a protocol for quantitative desorption of radiolabelled HOCs from SPME fibers using hexane was developed. Time series extractions indicated that loading of SPME fibers had reached steady-state by day 8 for PCBs 52, 77 and 153, phenanthrene, benzo[a]pyrene, *p,p'*-DDT and *p,p'*-DDE. The recovery of spiked radioactivity among the (residual) aqueous phase, the PDMS coating, and all remaining wetted experimental surfaces ranged between 80 and 120%. K_f values based on ^{14}C -labeled analogs were in good agreement with previously published values that were determined at (or closely approaching) equilibrium conditions and without significant chemical depletion and/or uncorrected system losses. Because it allows for the direct determination of HOCs associated with the residual aqueous and experimental surface compartments, the use of radiolabelled HOC analogs is a powerful tool in discriminating among competing sorptive compartments encountered in most SPME fiber calibration methodologies employed to date.

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1. Introduction

Since the introduction of solid-phase microextraction (SPME) as a quantitative analytical technique by Arthur and Pawliszyn [1] more than a decade ago, much has been published on its governing processes and potential environmental applications [2]. Successful implementation of SPME-based methodologies is strongly dependent upon accurate and reproducible determination of compound-specific partition coefficients (K_f s) that represent the steady-state distribution of target analyte between the SPME sorbent phase and the sample matrix. Whereas the precise determination of K_f values for volatile and/or water soluble organic compounds is relatively straightforward, corresponding exercises for hydrophobic organic chemicals (HOCs) have proven difficult because of their

inherently low water solubility and potential for experimental artifacts (i.e. non-environmental system losses) [3,4]. These difficulties are in part to blame for the wide range of reported K_f values, sometimes differing by an order of magnitude or more, for the same compound.

To date, only native HOCs have been used in pre-deployment calibration experiments to determine K_f s. Regardless of whether dynamic [5,6] or static methods [7,8] are employed, the accurate determination of K_f relies on knowledge of the truly dissolved aqueous phase concentration and the supposition of minimal system losses (a “closed mass balance”). A review of published fiber calibration techniques indicates that liquid–liquid extraction (LLE) is overwhelmingly used to obtain aqueous phase concentrations. For example, a static SPME procedure employing LLE was developed to determine the poly(dimethyl)siloxane (PDMS)–water K_f s for selected polychlorinated biphenyl congeners (PCBs) [9]. Although measured K_f values were reasonably consistent with those reported previously, the mass balance before and after SPME using PDMS

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fibers with various commercially available coating thicknesses ranged between 53 and 106%, and was particularly problematic for lower chlorinated congeners.

Incomplete mass balances can be attributed to several phenomena, including evaporation of more volatile analytes, random errors associated with analytical determinations and underestimation of HOC associated with the aqueous phase and/or system surfaces (i.e. glassware). A quantitative accounting of spiked material (i.e. a completed mass balance) in SPME fiber calibration protocols would serve to identify “sources” of hydrophobic analyte discrimination (e.g. glassware, septum and, stir bar surfaces), which to date have been more or less obscured. The use of radiolabelled HOC analogs, however, would allow for the direct determination of aqueous and system surface “loads” of the spiked compound, thus eliminating any potential artifacts and/or reducing uncertainty associated with indirect extraction efficiency dependent measurements (e.g. LLE). This study utilizes ^{14}C -labeled analogs in static aqueous phase extractions by SPME to determine K_f values for a select group of HOCs, including three PCB congeners, two DDT compounds and two polycyclic aromatic hydrocarbons (PAHs).

2. Materials and methods

2.1. Materials

EcoLite(+) scintillation fluid was obtained from ICN Biomedicals (Costa Mesa, CA, USA). ^{14}C -labeled 2,2',5,5'-tetrachlorobiphenyl (PCB 52), 3,3',4,4'-tetrachlorobiphenyl (PCB 77), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153), phenanthrene (PHEN), benzo[a]pyrene (BaP), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT) and 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene (*p,p'*-DDE) were purchased from Sigma (St. Louis, MO, USA). Aqueous solubility, spiking solution concentration, and initial spiked radioactivity for each test compound are shown in Table 1. Hexane (Ultra Resi-analyzed grade) and acetone (Optima grade) were supplied by Mallinckrodt Baker (Phillipsburg, NJ, USA) and Fisher Scientific (Pittsburgh, PA, USA), respectively. Distilled water with dissolved organic carbon (DOC) concentration <0.03 mg/L was used as the spiking medium.

2.2. Experimental

2.2.1. SPME extraction of ^{14}C -labeled analytes from spiked aqueous solutions

SPME fibers with 100- μm PDMS coating (Supelco, Bellefonte, PA, USA) were conditioned at 250 °C under a stream of ultra high purity helium (>99.999%) on a GC injection port for 0.5 h prior to initial use. Glass vials (25 mL) were washed with detergent and tap water, rinsed with distilled water, and kilned at 450 °C for ≥ 4 h. To determine the amount of ^{14}C -labeled HOC associated with glassware and stir bar (“system”) surfaces after SPME, 25-mL glass scintillation vials, prepared as described above, doubled as SPME fiber calibration vessels. PTFE-coated stirring bars were rinsed with double distilled water, sonicated in CH_2Cl_2 for 10 min, wrapped in solvent rinsed aluminum foil and dried in an oven at 100 °C.

Stock spiking solutions of ^{14}C analytes were prepared in acetone. Scintillation vials filled with 25 mL distilled water were then spiked with the appropriate volume of spiking solution. It should be noted that all analytes were spiked at concentrations that were less than their respective water solubilities for K_f determinations, except for PCB 153 whose spiked radioactivity corresponding to a saturated water solution is too low ($\sim 0.007 \mu\text{Ci}$) to determine reproducibly by liquid scintillation counting. To evaluate the potential implications of this level of spiked [^{14}C]PCB 153, K_f determinations for different initial spiked amounts (N_0) of PCB 153 were made. For N_0 values of 0.005, 0.016, 0.05, and 0.1 $\mu\text{Ci}/25 \text{ mL}$, measured $\log K_f$ values were 6.12 ± 0.04 , 6.23 ± 0.03 , 6.27 ± 0.15 , and 6.02 ± 0.15 , respectively. Thus, we concluded that the spike level chosen for [^{14}C]PCB 153 had no significant effect on the determination of K_f . A pre-cleaned stirring bar and 0.2 mg/mL analytical grade sodium azide (Mallinckrodt Baker) was added to each vial. A PTFE sheet and rubber bands were used to cover the vial opening to minimize gas exchange. After equilibration for 2 h, a SPME fiber was pierced through the PTFE sheet and exposed into the aqueous phase, and the vial placed on a magnetic stirrer (Corning, Corning, NY, USA) at 1000 rpm. All vials were wrapped with aluminum foil to minimize ambient light exposure and were kept at 23 ± 2 °C. At predetermined extraction times, the PDMS-coated fiber was carefully removed from the vial, shaken vigorously and gently wiped with a Kimwipe tissue

Table 1
Aqueous solubility and spike level for ^{14}C -labeled test compounds

Analyte	$C_{w,\text{sat}}^a$ (mg/L)	C_{spike}^b ($\mu\text{Ci}/\mu\text{mol}$)	N_{sat}^c (μCi)	N_0^d (μCi)
2,2',4,4'-Tetrachlorobiphenyl (PCB 52)	0.0153	7.2	9.4×10^{-3}	5.0×10^{-3}
3,3',4,4'-Tetrachlorobiphenyl (PCB 77)	0.012	12.7	6.2×10^{-4}	5.0×10^{-3}
2,2',4,4',5,5'-Hexachlorobiphenyl (PCB 153)	0.00095	12.6	8.4×10^{-4}	5.0×10^{-3}
1,1-Bis(4-chlorophenyl)-2,2-dichloroethene (<i>p,p'</i> -DDE)	0.0013	12.7	1.3×10^{-3}	1.2×10^{-3}
1,1,1-Trichloro-2,2-bis(<i>p</i> -chlorophenyl)ethane (<i>p,p'</i> -DDT)	0.003	12.8	2.7×10^{-3}	2.0×10^{-3}
Phenanthrene (PHEN)	1.15/1.29	55.7	9.0	5.0×10^{-3}
Benzo[a]pyrene (BaP)	0.0038	26.6	1.0×10^{-2}	5.0×10^{-3}

^a Aqueous water solubility at 25 °C [23–25].

^b Specific activity of stock spiking solution prepared in acetone.

^c Radioactivity corresponding to a saturated aqueous solution for 25 mL distilled water.

^d Initial spiked radioactivity for the determination of K_f values in 25-mL distilled water samples.

to remove residual water before being retracted into the syringe assembly.

2.2.2. Solvent desorption of HOCs extracted onto SPME fibers

A mixture of native PCB 52 and PCB 153 (AccuStandard, New Haven, CT, USA) was used to develop a protocol for quantitative recovery of ^{14}C analytes sorbed to SPME fibers. 100- μm PDMS fibers in triplicate were inserted into distilled water spiked with native HOCs for 24 h. Two fibers were transferred into 10-mL aliquots of a single or binary solvent system—100% acetone, 100% hexane, or a 1:1 (v/v) mixture of the two above solvents and sonicated for 1–24 h. Fibers after solvent desorption were injected directly into the GC/MS (Section 2.3.1) to obtain the carryover response (A_c). The third fiber from each spiked vial was thermally desorbed in GC/MS injector (without any solvent desorption) to determine the original loading response (A_0). The HOC-fiber carryover ratio, or A_c/A_0 , plotted versus time was used to select the most efficient desorption protocol, which was 2 h sonication in 100% hexane (see also Section 3). Further experimentation indicated that extending the fiber sonication period by 30 min reduced carryover by less than 0.1%.

2.2.3. Determination of HOC sorption to glassware

To assay radioactivity sorbed to glassware and stir bar surfaces after removal of the SPME fiber and residual aqueous solution, 25-mL hexane was added to each calibration vial after the residual aqueous contents had been removed, the vial/stir bar sonicated for 3 h, and left to soak at room temperature overnight. A 10-mL aliquot of the hexane extraction solution was then solubilized in 10 mL scintillation cocktail and counted using the LSC as described in Section 2.3.2.

2.2.4. Determination of HOC-SPME fiber equilibration times

To ensure that steady state distributions of ^{14}C analytes were achieved using the protocols described above, a time series of SPME extractions for ^{14}C -labeled PCB 52, PCB 153 and BaP was performed. These compounds span a wide range of hydrophobicities for our study HOCs (Table 1). A clean SPME fiber was placed in individual 25-mL glass vials containing 0.05 $\mu\text{Ci}/25\text{ mL}$ for PCB 52 and 153, and 0.01 $\mu\text{Ci}/25\text{ mL}$ for BaP. Triplicate fibers were removed from spiked solutions at 1, 2, 4, 8 and 16 days, desorbed into hexane as described in Section 2.2.2, and analyzed by LSC (Section 2.3.2). The time to equilibrium (t_{eq}) was determined from analyte-specific plots of K ($K = C_f/C_w$) versus time, where C_f and C_w are the analyte concentrations in SPME fiber and the aqueous phase after SPME, respectively).

2.3. Instrumental analysis

2.3.1. GC/MS analysis

Analyses of native HOCs 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

8200 autosampler. A 60 m \times 0.25 mm i.d. with 0.25 μm film thickness DB-5 fused silica column (J&W Scientific/Agilent Technologies, Folsom, CA, USA) was used for chromatographic separation. After a 1 min hold at 100 $^\circ\text{C}$, the column temperature was increased to 220 $^\circ\text{C}$ at 8 $^\circ\text{C}/\text{min}$, followed by a second increase at 10 $^\circ\text{C}/\text{min}$ to 290 $^\circ\text{C}$ (10 min hold). Ultrahigh purity helium at a constant flow of 1.3 mL/min was the carrier gas. Injector temperature was held constant at 280 $^\circ\text{C}$. Full scan (m/z 100–400) mass spectra were acquired in the positive electron impact mode at 70 eV. The temperatures of the ion trap, manifold, and transfer line temperature were maintained at 220, 80, and 280 $^\circ\text{C}$, respectively.

2.3.2. Radioactivity assay

All ^{14}C -labeled analytes were counted using a 1214 RackBeta 'Excel' liquid scintillation counter (LKB Wallac, Wallac, Turku, Finland). To determine the radioactivity in residual spiked water after SPME extraction, a 5-mL aliquot was transferred into a clean glass scintillation vial with EcoLiteTM(+) scintillation cocktail for counting. The hexane solution used to desorb HOCs from SPME fibers and glassware/stir bar (Section 2.2.2) was also solubilized in scintillation cocktail for counting. Radioactivity of spiked water after SPME (N_w), glassware and stir bar adsorption (N_s), and SPME fiber sorption (N_f) were compared to standards of known activities and corrected for quenching, background and physical decay of the tracer. Counting times were adjusted to obtain counting rates with relative errors of 10% or less.

2.4. Data analysis

2.4.1. HOC mass balance and distribution among experimental compartments

The distribution of a HOC among experimental compartments, including the PDMS coating associated with the SPME fiber, is governed by the law of mass balance. The other interacting phases (as defined in previous papers) include aqueous, air (headspace) and container surfaces. The initial (i.e. spiked) HOC amount (N_0) before SPME in a closed system described above is equal to the sum of the amounts in individual phases after SPME is complete, i.e.

$$N_0 = N_w + N_f + N_s + N_h + N_{\text{DOC}} \quad (1)$$

where subscripts w, f, s, DOC, and h designate water, SPME fiber, solid, dissolved organic carbon and headspace, respectively.

In natural waters, DOC may be an important binding medium for HOCs [10]. The freely dissolved fraction (f_{fd}) of a chemical can be estimated from the three-phase partitioning model [11,12]:

$$f_{\text{fd}} = \frac{1}{(1 + C_{\text{POC}}K_{\text{POC}} + C_{\text{DOC}}K_{\text{DOC}})} \quad (2)$$

where C_{POC} and C_{DOC} are the concentrations of particulate organic carbon (POC) and DOC, respectively; and K_{POC} or K_{DOC} is the partition coefficient between POC or DOC and the freely dissolved chemical. With a measured DOC of less than

0.03 mg/L and $POC \approx 0$ in distilled water used in this study, and further assuming that $K_{DOC} = 0.08 K_{ow}$ [12], the corrected $\log K_f$ values were not significantly different compared with all $\log K_f$ values before correction. This was true even for PCB 153, which has the highest $\log K_{ow}$ value among the target analytes. Therefore, the amount of HOC associated with DOC (N_{DOC}) was negligible.

Since their vapor pressures are typically very low, the effect of headspace has been shown to be insignificant for hydrophobic chemicals [13]. In contrast, HOCs have a strong affinity for solid surfaces, including plastic, metal, and even the glass and PTFE used in this experiment [14–16]. Non-quantitative recoveries of very hydrophobic compounds such as five- and six-ring PAHs [17] and PCBs [18] were reported with SPME extraction using glass containers (regardless of silanization) and stir bars. Therefore, we assume that adsorption of HOCs by glassware and stir bars are similar in nature and extent. As a result, $N_h = N_{doc} \approx 0$, and the general mass balance of Eq. (1) becomes

$$N_0 = N_w + N_s + N_f \quad (3)$$

Therefore, the total recovery of HOC (R_t) in a three-compartment system can be expressed as

$$R_t = \frac{(N_w + N_s + N_f)}{N_0} \times 100 \quad (4)$$

As described in Section 2, the initial (spiked) radioactivity associated with the chemical spike (N_0), also spiked into 1-mL of distilled water and assayed by LSC, was used to calculate R_t using Eq. (4). In addition, the relative mass distribution of analytes in each of the three compartments is represented by

$$i\% = \frac{N_i}{N_0} \times 100 \quad (5)$$

where $i\%$ represents the relative mass distribution in water, glassware or SPME fiber.

2.4.2. Determination of K_f values

After determination of t_{eq} for each of the seven study HOCs (see Section 2.2.4), spiked water samples were prepared in 25-mL glass vials containing radioactivity associated with each spiked compound (Table 1). As with the time series experiment, additions of total radioactivity were kept below levels that would exceed corresponding water solubilities, except for PCB 153. SPME fibers were exposed as described previously with extraction times of 4 days for PHEN, BaP, PCB 52 and PCB 77; and 8 days for PCB 153, p,p' -DDT and p,p' -DDE. The absolute analyte amount (N_f^∞) extracted by the SPME fiber and the analyte amount in aqueous phase (N_w^∞) after SPME were calculated from the external calibration curve established by LSC. K_f can then be expressed as

$$K_f = \frac{C_f^\infty}{C_w^\infty} = \frac{N_f^\infty V_w}{V_f N_w^\infty} \quad (6)$$

where C_f^∞ and C_w^∞ are the analyte concentrations in the PDMS coating and residual spiked water at equilibrium, respectively;

and V_f and V_w are the volumes of the PDMS coating and counted (spiked) water, respectively.

3. Results and discussion

3.1. Optimization of mass balance protocols

3.1.1. SPME fiber desorption

The carryover ratio (A_c/A_0) for native surrogates PCB 52 and PCB 153 decreased with increasing desorption/sonication time for all three solvent systems (Fig. 1). Hexane (100%) achieved the best overall performance, with less than 2% carryover for both surrogate congeners after 1 h compared with >4% for the acetone/hexane (1:1, v/v) mixture and >6% for 100% acetone (PCB 153 data only). Whereas the time dependent carryover for PCB 52 was similar between 100% hexane and the acetone/hexane mixture, 100% hexane clearly desorbed greater amounts of PCB 153 over the entire time range evaluated. Acetone demonstrated the poorest performance of the three solvent systems, with 1–2% carryover after 3 h. Assuming that the two test compounds (PCBs 52 and 153) represented the extremes in terms of extractability from SPME for all study

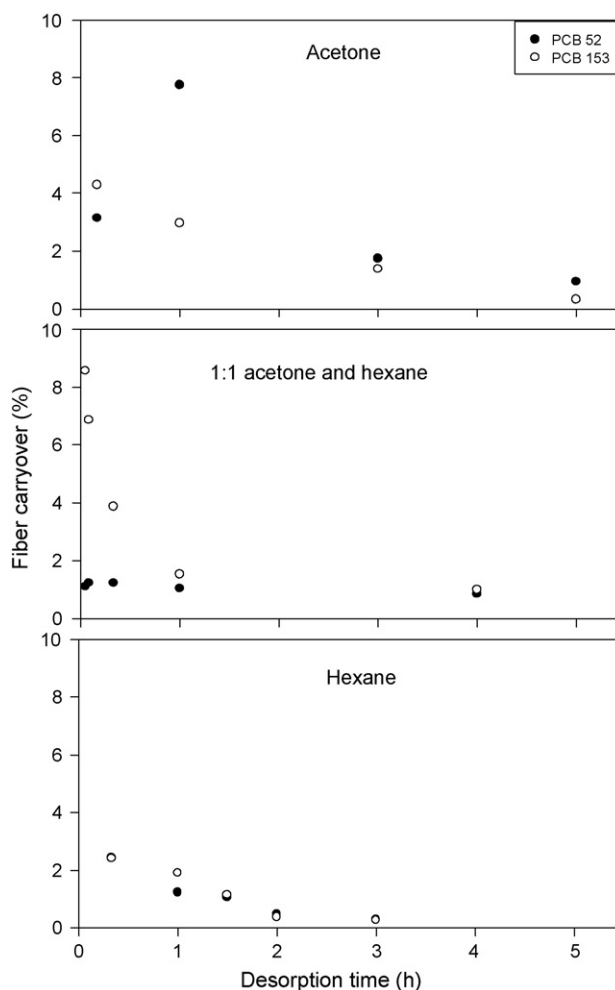


Fig. 1. Percent carryover ($A_c/A_0 \times 100$) of PCB 52 and PCB 153 vs. sonication time for SPME fibers extracted by different organic solvent systems.

compounds, a protocol employing 100% hexane and a 2 h desorption/sonication time was adopted. Furthermore, the carryover of ^{14}C -labeled chemicals was minimized by exposing the SPME fiber in hexane for an additional 1 h after sonication. Analysis by LSC after this treatment indicated that carryover was less than 0.5% for all analytes.

The SPME fiber manufacturer recommends not exposing PDMS coatings to nonpolar solvents due to polymer swelling (and a resultant alteration of coating volume). To circumvent these concerns, we removed the integrative fiber cap after fiber desorption (in hexane) was complete, and did not retract the fiber into the accompanying syringe until complete evaporation of hexane. To test for detrimental effects of hexane exposure, the same fiber was subject to 6 cycles of aqueous phase sorption/hexane desorption/sonication using a solution containing all seven target analytes except PCB 77 (Table 1) in their native form. The extraction efficiency did not decrease with increasing number of cycles, with relative standard deviation of MS response being 17.3, 25.6, 19.5, 10.0, 17.1, and 25.2% ($n=6$) for PCB 52, PCB 153, phenanthrene, BaP, p,p' -DDE, and p,p' -DDT, respectively. Accordingly, SPME fibers were employed for a maximum of 6 cycles in this study.

3.1.2. Glassware and stir bar cleaning method

It was anticipated that adsorption of ^{14}C -labeled HOCs would be measurable by LSC, the extent of which would be a function of hydrophobicity. Therefore, the most hydrophobic target compound (PCB 153) was selected to optimize this method. Initially, the scintillator (Ecolite) was added directly into vials emptied of spiked water to estimate N_s (Eq. (3)). This resulted in a total PCB 153 recovery rate of $\sim 50\%$, even as the vials were left overnight to equilibrate with the scintillation fluid. To more efficiently solve the adsorbed HOC from glass and stir bar surfaces, 2-mL hexane was added to the emptied vials and shaken vigorously by hand. The total recovery improved to $\sim 70\%$ but that was not enough to be considered quantitative. Finally, a full volume of hexane (~ 25 mL) was first sonicated in the emptied vial for 3 h, and then left for 24 h before counting. With a total recovery rate ranging between 80 and 120%, this final method was adopted for determining the amount sorbed to experimental container surfaces (N_s).

3.2. Determination of time to equilibrium

As expected, the sorption of ^{14}C -labeled PCB 52, PCB 153, and BaP to the PDMS coated SPME fiber (represented by K) increased with increasing extraction time (Fig. 2). Whereas maximum K values for PCB 52 and BaP were achieved after 4 days, the corresponding value for PCB 153 was achieved at day 8. This is in accordance with the direct proportionality between molecular weight (MW) and hydrophobicity (as measured by K_{ow}) for HOCs [19]. Since the MW and K_{ow} for all other target analytes in Table 1 are less than that for PCB 153, it follows that all analytes should reach steady state within 8 days. Based on similarities of these properties with those evaluated in the time series (i.e. PCB 52, PCB 153 and BaP), the time to equi-

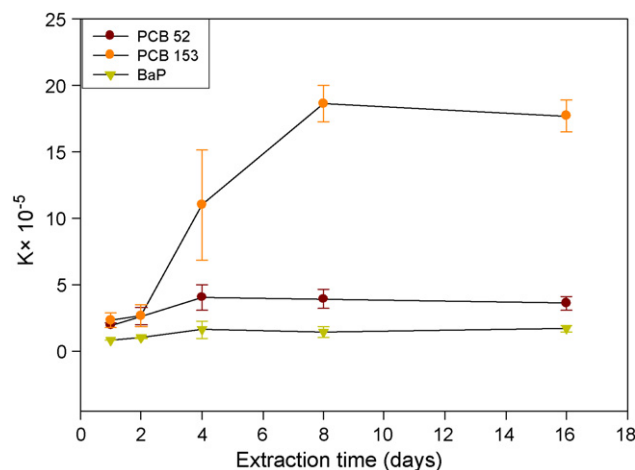


Fig. 2. The C_f/C_w ratio (K) of selected ^{14}C -labeled analytes vs. extraction time using 100 μm PDMS coated SPME fibers and initial spikes of 0.05 μCi for PCB 52 and PCB 153 and 0.01 μCi for BaP.

librium for PHEN and PCB 77 was chosen as 4 days, and that for p,p' -DDT and p,p' -DDE was selected as 8 days.

3.3. Mass balance determinations

Total mass recovery (R_t) in the three experimental compartments for ^{14}C -labeled PCB 52, PCB 153 and BaP was greater than 90% for all time determinations. The lone exception to these quantitative recoveries was the $\sim 80\%$ recovery for PCB 52 at 16 days extraction (Fig. 3). It is interesting to note that although the absolute percentages for the aqueous and container surface compartments of [^{14}C]PCB 52 did not change with time, the fiber fraction appeared to decrease to $\sim 60\%$ at day 16 suggesting loss (desorption) into the aqueous phase. However, since the aqueous or container surface fractions did not show a concomitant increase, the most plausible explanation for this loss was evaporation—an irreversible loss for these systems that was not measured. Thus, it is important to understand the implications of conducting fiber calibration experiments for an unnecessarily long time for compounds in which loss via headspace is possible.

Discrimination among system compartments afforded by this technique also revealed a time dependent distribution for [^{14}C]PCB 153, the most hydrophobic analyte tested. Initially, as much as 10% of the total radioactivity was present in the aqueous phase, a fraction that decreased to $<5\%$ by day 4 and thereafter (Fig. 3). Conversely, the PDMS coating fraction steadily increased with time whereas the fraction associated with container surfaces decreased. These data suggest two processes at work, the first occurring between days 0 and 4 amounting to a redistribution from the aqueous phase due to the initial “overspiking” (see Section 2.2.1) of the radiolabelled analog. The redistribution of [^{14}C]PCB 153 from container surfaces to the PDMS coated SPME fiber occurring throughout the 16 day extraction, on the other hand, illustrates the hydrophobic (K_{ow}) effect on diffusion rate into the PDMS (fiber) phase.

The quantitative (80–100%) recoveries observed herein are in contrast to those previously obtained for native PCB congeners using methods described in our previous work [9]. For

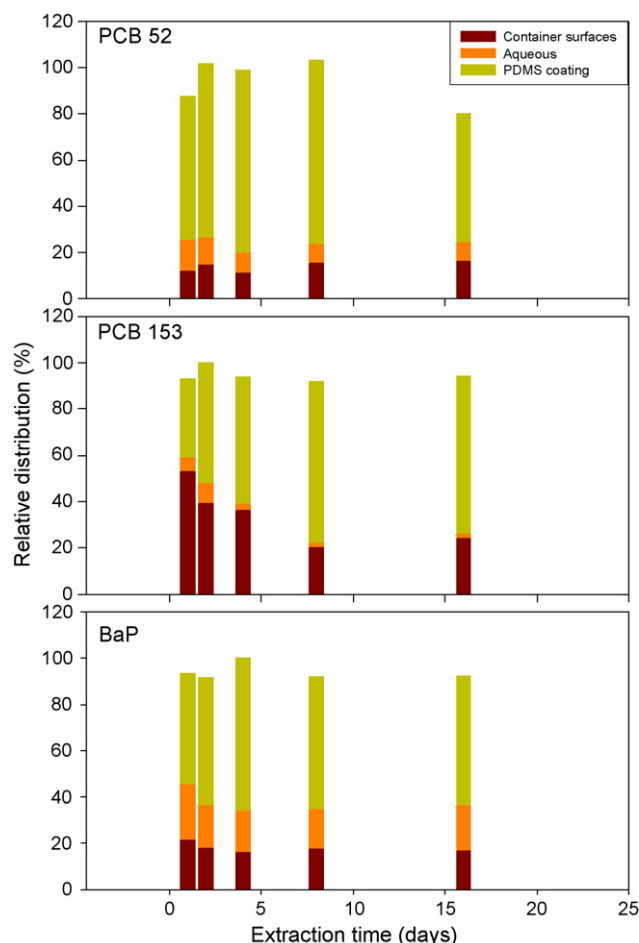


Fig. 3. The relative distribution among container, aqueous and PDMS coating phases and total recovery (R_t) of spiked radioactivity for selected ^{14}C -labeled analytes. Initial radioactivity was $0.05\ \mu\text{Ci}$ for PCB 52 and PCB 153, and $0.01\ \mu\text{Ci}$ for BaP.

example, the average R_t values for PCB 47 (a tetrachloro isomer of PCB 52) and PCB 153 were 57.4 and 67.5% after 100- μm PDMS coating 20 days extraction, respectively. In addition to the aforementioned likelihood of evaporative loss for the lighter homologs (PCBs 47 and 52), these differences can be attributed to losses associated with liquid–liquid extraction for aqueous phase HOCs and errors associated with GC/MS quantification ($\pm 20\%$ error). Thus, in addition to quantification of the multi-compartment distribution, a greater degree of mass balance was achieved using radiolabelled homologs.

3.4. Comparison of kinetic profile

Time series data from a previous study [9] using native congeners (PCBs 47 and 153) were plotted against those for the corresponding ^{14}C -labeled analog. However, ^{14}C]PCB 52 (and not ^{14}C]PCB 47) serves as the comparative tetrachloro analog since ^{14}C]PCB 47 was not commercially available. K values for native PCBs 47 and 153 reached apparent steady state after 8 and 16 days extraction, whereas the corresponding times for ^{14}C]PCB 52 and ^{14}C]PCB 153 were 4 and 8 days (Fig. 4). Also,

equilibrium K values for PCB 153 at day 16 were nearly identical, but this was not the case for ^{14}C]PCB 52 and native PCB 47. There are several possible explanations for these discrepancies. Because the volume of spiked aqueous media (i.e. HOC reservoir available for sorption by SPME) was much smaller (25 mL) in this study compared with the 130-mL test volume employed in our former work [9], depletion in the aqueous phase may have occurred over time. This explanation, however, does not apply to PCB 153 and was not supported using mass balance considerations (Fig. 3). Another difference between the two studies is the higher uncertainty associated with LLE and GC/MS quantitation, as suggested by the larger error bars for the native study (Fig. 4). Thirdly, losses were most likely not identical between the two SPME fiber calibration systems even though attempts were made to standardize glassware, septa, stir bars, etc. [20,21]. Whereas glass flasks were silanized before use in the native study [9], disposable, non-silanized glass vials were used in the present study as we have found that silanization has little/no effect on adsorption. In fact, silanization may lead to higher variability than anticipated, and may have contributed to the greater variability in “native” K values. Lastly, the initial spiked radioactivity for ^{14}C]PCB 153, which was \sim six-fold higher than its expected water solubility (Table 1), may have

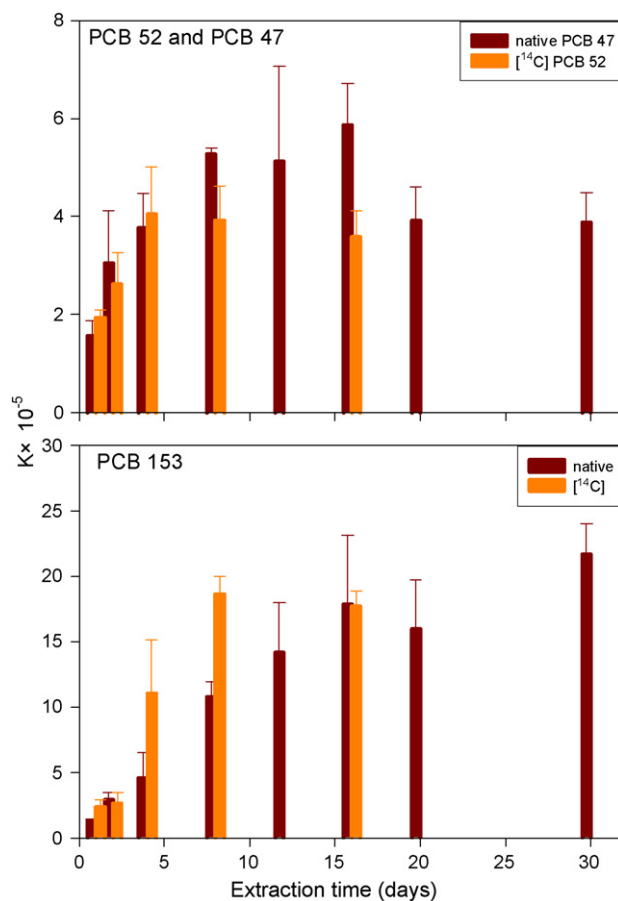


Fig. 4. Time series of C_f/C_w ratio (K) for ^{14}C -labeled (this study) vs. native PCB congeners. Note that data for native PCB 47 and ^{14}C]PCB 52 are plotted together.

Table 2
Comparison of log K_f values for selected hydrophobic organic chemicals (HOCs)

Compound	log K_{ow} ^a	¹⁴ C (this study)	Native ^d	Mayer et al. [7]		Poerschmann et al. [6]			Paschke and Popp [8]		Zeng et al. [22], 12 days
				3 days	42 days	24 h	24 h	96 h	7 μ m	100 μ m	
PCB 52	5.84 ^a	5.30 (0.07)	5.52 (0.09)	5.30 (0.07)	5.38 (0.01)	4.48	5.21	5.55	4.98	5.14	5.49 (0.06)
PCB 77	6.63 ^a	5.81 (0.30)									5.80 (0.04)
PCB 153	6.76 ^a	6.12 (0.04)	6.25 (0.09)	5.84 (0.08)	6.16 (0.09)	4.41	5.63	6.05	6.01	5.67	5.45 (0.10)
<i>p,p'</i> -DDE	6.96 ^b	5.85 (0.10)	6.17 (0.07)	5.73 (0.09)	5.88 (0.05)				5.39	5.26	5.88 (0.05)
<i>p,p'</i> -DDT	6.61 ^b	5.56 (0.05)									5.63 (0.10)
PHEN	4.57 ^c	4.45 (0.12)	3.90 (0.07)	4.01	3.98						
BaP	6.04 ^c	4.95 (0.13)	5.75 (0.29)			4.9	5.19				4.26 [26]

[7] Static mode, 90 mL (3 days) and 900 mL (42 days) sample sizes, 100 ng/L spiking concentration; [6] static (24 h) mode, 4- and 250-mL sample volumes, 50 and 500 ng/L spiking concentrations, respectively, dynamic (96 h) mode, concentration not reported; [8] static mode, 480 mL sample size, 100–200 ng/L spiking concentrations; [22] static mode, 1600 mL sample size, 50 ng/L spiking concentration; [26] static mode, 38 mL sample size, 1 ng/mL spiking concentration.

^a From Ref. [27].

^b From Ref. [28].

^c From Ref. [29].

^d Yang et al. unpublished results, 130 mL sample size, 1 ng/mL spiking concentration.

influenced the initial stages of fiber–water–glassware partitioning (see also Section 3.3). Excess radiolabelled compound may have partitioned rapidly to the fiber, temporarily “overloading” the PDMS coating resulting in higher than expected K values (days 4 and 8, Fig. 4). After day 8, however, the system had corrected for this excess amount and established a steady state that was equivalent to that observed with the native system.

3.5. Comparison of K_f values from previous studies

Although previously published values of K_f vary widely for the same HOC (Table 2), the values determined using radiolabelled analogs in this study agreed well with several reports that used native compounds. For example, log K_f for [¹⁴C]PCB 52 (this study) was identical (5.30 ± 0.07) to that reported by Mayer et al. [7] for a 3 day extraction, and fell within 0.2 log units of values reported by Poerschmann et al. [6], Paschke and Popp [8] and Zeng et al. [22]. Log K_f for [¹⁴C]PCB 153 (6.12 ± 0.04 , this study) was less than or equal to 0.1 log units of values reported by three of the five investigators in Table 2. Log K_f s for ¹⁴C-labeled PCB 77 (5.81 ± 0.30) and *p,p'*-DDT (5.56 ± 0.05) were within 0.01 and 0.07 log units of values reported by Zeng et al. (5.80 ± 0.04) and (5.63 ± 0.10), respectively [22]. For *p,p'*-DDE, our value (5.85 ± 0.10) was within 0.03 log units of those reported by Mayer et al. [7] and Zeng et al. [22]. Lastly, for BaP, our value of 4.95 ± 0.13 was within the range of 4.9–5.19 reported by Paschke and Popp [8]. Our values were in general several fold greater than those reported using short extraction times (≤ 3 days), a difference exacerbated for the more hydrophobic test compounds (e.g. PCB 153). In contrast, log K_f values of all ¹⁴C-labeled chemicals except for PHEN were lower than those reported for corresponding native compounds using our previously described method [9], also noting that no log K_f values of native *p,p'*-DDT and PCB 77 were measured. These differences likely stem from the unaccounted losses (60–80% R_t) and greater (GC/MS) analytical uncertainty associated with the native congener determinations, and underscore the

utility of the more sensitive, precise radiolabelled analogs technique.

Our results largely confirmed values determined under equilibrium conditions reported previously for HOCs with very limited K_f data, e.g. the DDTs and PCBs (Table 2). This was more difficult to assess for PAH, as the data available for comparison were extremely sparse, our determination for BaP (4.95 ± 0.13) comparing well with that reported by Paschke and Popp [8] (4.9–5.19) not withstanding. Future experiments characterizing K_f values for additional PAH under different test conditions are thus sorely needed.

The relationships between log K_f and log K_{ow} have often been used to judge whether the underlying SPME process is absorption (linear) or adsorption (nonlinear) [6]. The square of linear correlation coefficient for the selected HOCs in this study was 0.852, with no apparent deviation from linearity since no very hydrophobic chemicals were included (the highest log K_{ow} value was less than 7). Therefore, the results from the present study support the absorption theory for SPME sorption of HOCs using the PDMS coating.

4. Conclusions

These data serve as validation for several published reports of HOC-SPME distribution ratios under steady-state extraction conditions, and underscore the importance of careful determination of K_f values. It has been shown that a complete mass balance and knowledge of the time to equilibrium for each HOC-SPME fiber (thickness) system are critical for understanding the results of SPME fiber calibration protocols. Although impractical for routine calibration procedures, the use of radiolabelled analogs can be selectively employed to quantitatively define the distribution of a chemical component among multiple compartments, such as those encountered using SPME. This approach is particularly powerful for HOCs that inherently exhibit very low concentrations and mass inventories in simple and/or complex liquid phases, e.g. a natural water system or biological fluids such as blood plasma or urine.

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References

- [1] C.L. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145.
- [2] J. Pawliszyn, *Solid Phase Microextraction: Theory and Practice*, Wiley-VCH, New York, NY, 1997.
- [3] S.-C. Lung, Y. Yanagisawa, T.E. Ford, J.D. Spengler, *Chemosphere* 41 (2000) 1857.
- [4] W.H.J. Vaes, P. Mayer, A.G. Oomen, J.L.M. Hermens, J. Tolls, *Anal. Chem.* 72 (2000) 639.
- [5] B. Shurmer, J. Pawliszyn, *Anal. Chem.* 72 (2000) 3660.
- [6] J. Poerschmann, T. Górecki, F.-D. Kopinke, *Environ. Sci. Technol.* 34 (2000) 3824.
- [7] P. Mayer, W.H.J. Vaes, J.L.M. Hermens, *Anal. Chem.* 72 (2000) 459.
- [8] A. Paschke, P. Popp, *J. Chromatogr. A* 999 (2003) 35.
- [9] Z.-Y. Yang, E.Y. Zeng, H. Xia, J.-Z. Wang, B.-X. Mai, K.A. Maruya, *J. Chromatogr. A* 1116 (2006) 240.
- [10] C.T. Chiou, R.L. Malcolm, T.I. Brinton, D.E. Kile, *Environ. Sci. Technol.* 20 (1986) 502.
- [11] Y.-P. Chin, P.M. Gschwend, *Environ. Sci. Technol.* 26 (1992) 1621.
- [12] L.P. Burkhard, *Environ. Sci. Technol.* 34 (2000) 4663.
- [13] E.Y. Zeng, J.A. Noblet, *Environ. Sci. Technol.* 36 (2002) 3385.
- [14] Y. Yang, D.J. Miller, S.B. Hawthorne, *J. Chromatogr. A* 800 (1998) 257.
- [15] E. Baltussen, P. Sandra, F. David, H.-G. Janssen, C. Cramers, *Anal. Chem.* 71 (1999) 5213.
- [16] Y. Yang, S.B. Hawthorne, D.J. Miller, Y. Liu, M.L. Lee, *Anal. Chem.* 70 (1998) 1866.
- [17] V.M. León, B. Álvarez, M.A. Cobollo, S. Muñoz, I. Valor, *J. Chromatogr. A* 999 (2003) 91.
- [18] T. Benijts, J. Vercammen, R. Dams, H.P. Tuan, W. Lambert, P. Sandra, *J. Chromatogr. B* 755 (2001) 137.
- [19] R. Schwarzenbach, *Environmental Organic Chemistry*, Wiley, New York, 1993.
- [20] T. Górecki, J. Pawliszyn, *Analyst* 122 (1997) 1079.
- [21] T. Górecki, A. Khaled, J. Pawliszyn, *Analyst* 123 (1998) 2819.
- [22] E.Y. Zeng, D. Tsukad, J.A. Noblet, J. Peng, *J. Chromatogr. A* 1066 (2005) 165.
- [23] T. Öberg, *Int. J. Chem.* 14 (2001).
- [24] D. Mackay, W.Y. Shiu, *J. Chem. Eng. Data* 22 (1977) 399.
- [25] J.C. Prager, *Environmental Contaminant Reference Databook*, Wiley, New York, 1998.
- [26] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, *Anal. Chem.* 68 (1996) 144.
- [27] D.W. Hawker, D.W. Connell, *Environ. Sci. Technol.* 22 (1988) 382.
- [28] J. De Bruijn, F. Busser, W. Seinen, J. Hermens, *Environ. Toxicol. Chem.* 8 (1989) 499.
- [29] J.M. Neff, W.A. Burns, *Environ. Toxicol. Chem.* 15 (1996) 2240.