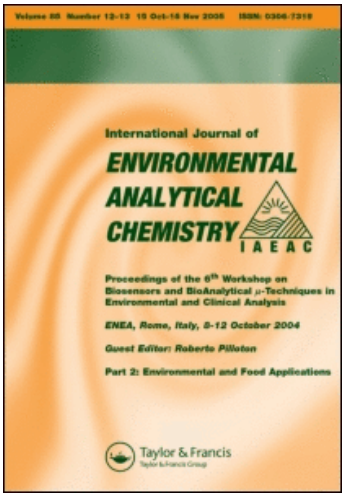

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The use of solid-phase microextraction to rapidly measure dissolved PCBs in natural waters

Abby R. Schneider[a]; Alessandra Paolicchi[a]; Joel E. Baker[a]
[a] Chesapeake Biological Laboratory, University of Maryland, Solomons, MD 20688, USA

To cite this Article Schneider, Abby R. , Paolicchi, Alessandra and Baker, Joel E.(2006) 'The use of solid-phase microextraction to rapidly measure dissolved PCBs in natural waters', International Journal of Environmental Analytical Chemistry, 86: 11, 789 — 803
To link to this Article: DOI: 10.1080/03067310600635376
URL: http://dx.doi.org/10.1080/03067310600635376

Intern. J. Environ. Anal. Chem.
Vol. 86, No. 11, 15 September 2006, 789–803

Taylor & Francis
Taylor & Francis Group

The use of solid-phase microextraction to rapidly measure dissolved PCBs in natural waters

ABBY R. SCHNEIDER, ALESSANDRA PAOLICCHI and JOEL E. BAKER*

Chesapeake Biological Laboratory, University of Maryland, 1 Williams Street, Solomons, MD 20688, USA

(*Received 18 August 2005; in final form 23 January 2006*)

A method to measure dissolved polychlorinated biphenyls (PCBs) in natural waters on 30 min time frames using negligible depletion non-equilibrium solid-phase microextraction (SPME) was developed with detection limits ranging from 0.6 to 5.2 ng L^{-1}. SPME fibres made from optical cable were inserted into a glass tube and attached to the shaft of a motor that revolved at 130 rpm to move the SPME fibres through the sampled water at a constant rate. To test for matrix interferences, measurements were made in three solutions with the same known dissolved PCB concentration but different matrices. Dissolved PCB measurements made in the presence of 8 mg L^{-1} of DOC and 200 mg L^{-1} of suspended solids were not significantly different from measurements made in deionized water, demonstrating that neither matrix interfered with SPME measurements of dissolved PCBs. PCB concentrations measured by XAD-2 resin extraction were greater than SPME measurements, suggesting that XAD measurements included DOC-associated PCBs.

Keywords: SPME; PCBs

1. Introduction

Despite the fact that hydrophobic organic contaminants (HOCs) in natural waters are primarily bound to particles and colloids, the dissolved phase is the most bioavailable to aquatic organisms and even low dissolved concentrations (i.e. pg L^{-1}) are important [1]. Historically, measuring dissolved concentrations of HOCs in natural waters has been time-consuming and expensive. Traditional methods involve filtering large volumes of water to remove particles, passing the filtrate through a resin, and then extracting the resin [2, 3]. Small particles and colloids may pass through the filters and be included in the dissolved measurement.

Passive sampling devices (PSDs) were developed as an inexpensive and practical alternative to traditional water sampling methods. For example, semi-permeable membrane devices (SPMDs) are designed to mimic organism exposure by measuring

*Corresponding author. Fax: +1-410-326-7341. Email: baker@cbl.umces.edu

International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310600635376

only the dissolved or bioavailable HOCs. SPMDs are polyethylene tubing containing model lipids, and only dissolved HOCs pass through the membrane and partition into the lipid [4]. Rates of uptake of HOCs into SPMDs depend on the surface area of the SPMD, the thickness of the boundary layer surrounding the SPMD, and the diffusion coefficient of the HOCs [5]. Rantalainen *et al.* [6] found that uptake rates for polychlorinated biphenyls (PCBs) into SPMDs range from 50 to 95 L/m^2/day. Therefore, SPMDs need to be deployed in aqueous environments for several days to obtain a sufficient mass for HOC analysis using standard extraction and analytical techniques. Such PSDs cannot capture short-term variability in dissolved concentrations.

Pawliszyn and colleagues first developed the principles of solid-phase microextraction (SPME) to allow more rapid measurements of dissolved organic chemicals [7]. SPME is an analytic technique in which a fused silica rod coated with a polymer such as polydimethylsiloxane (PDMS) is exposed to the aqueous environment. Dissolved HOCs diffuse from the water into the polymer coating, and the fibre is then directly injected into the gas chromatograph (GC) for analysis. Diffusion into the SPME fibre is much faster than diffusion into other passive sampling devices because of its small size. However, HOCs can take anywhere from hours to days to reach equilibrium, with the SPME fibre depending on the extraction conditions [8–10].

The rate of diffusion into the SPME fibre depends on the thickness of the polymer coating, the diffusion coefficient of the analyte in water, and the thickness of the boundary layer or unstirred water layer (UWL) between the SPME fibre and the water [7]. The rate-limiting step in this process is diffusion through the UWL surrounding the SPME fibre [9]. Agitating or stirring the water sample reduces the thickness of this layer. Various methods, such as a magnetic stirring, vortex mixing, and sonication are used, and each has its own advantages and disadvantages [11, 12]. For example, Yang *et al.* [10] was able to reduce the time for dissolved PCBs to reach equilibrium with the SPME fibre to less than 5 h by continuously agitating the samples with a magnetic stir bar. However, the PCBs also absorbed onto the magnetic stir bar and were removed from the system. The various agitation techniques decrease the time it takes high-molecular-weight HOCs to reach equilibrium from days to hours [9, 10, 13]. However, this timescale is still not fast enough to measure short-term variations in dissolved concentrations. Additionally, none of the current techniques provide agitation to SPME fibres deployed directly into natural waters.

Non-equilibrium SPME is used to conduct more rapid measurements of dissolved concentrations. In this technique, the SPME fibre is exposed to a sample just long enough to be able to readily detect the higher-molecular-weight compounds, typically 20–90 min [14–16]. In order to quantify the concentration of HOCs on the fibres, the exposure time and mixing conditions are kept constant for all samples and external calibration solutions [15, 17, 18]. This technique is less sensitive than the equilibrium technique but measures HOC concentrations on shorter timescales. Negligible depletion SPME assumes that the amount of HOCs extracted from the aqueous solution does not appreciably change the dissolved concentration with time, and therefore equilibrium distributions to particles are not disturbed. If other components of the sample do not interfere with the kinetics of uptake onto the SPME fibre, a one-compartment kinetic

model describes the uptake of dissolved chemical onto the SPME fibres before equilibrium is reached [19].

$$\frac{\mathrm{d}[X]_{\mathrm{SPME}}}{\mathrm{d}t} = k_1[X]_{\mathrm{d}} - k_2[X]_{\mathrm{SPME}}, \tag{1}$$

where $[X]_{\mathrm{SPME}}$ is concentration on the SPME fibre (mass/volume), $[X]_{\mathrm{d}}$ is the dissolved concentration (mass/volume), and k_1 and k_2 are rate constants (1/time) representing the uptake and release of X from the SPME fibre coating. At equilibrium the concentration of X on the SPME fibre is defined by a constant K_{SPME}

$$K_{\mathrm{SPME}}(X) = \frac{k_1}{k_2} = \frac{[X]_{\mathrm{SPME,EQ}}}{[X]_{\mathrm{d}}}. \tag{2}$$

Integrating equation (1) gives an equation for the concentration on the SPME fibre at any given time t assuming that the dissolved concentration does not change with time [20].

$$[X]_{\mathrm{SPME},t} = \frac{k_1}{k_2}[X]_{\mathrm{d}}\left(1 - e^{-k_2 t}\right). \tag{3}$$

In order to use negligible depletion non-equilibrium SPME to measure dissolved concentrations of HOC, other matrices present in the water must not interfere with the rate uptake of dissolved HOCs into the SPME fibres. That is, the presence of suspended solids, dissolved organic carbon, and other material in the water column must not influence the partitioning of HOCs into the SPME fibre. Several studies have examined this issue in detail and found matrix effects to be negligible for suspended solids concentrations ranging from 20 to 1000 mg L^{-1} [13, 15, 20–22]. However, these studies focused on a single compound, and the impact of matrix effects needs to be tested more thoroughly for a wider range of compounds.

In this study, we present a method using negligible depletion non-equilibrium SPME to measure mono- through penta-chlorinated dissolved PCB congeners in natural waters on 30 min time frames. Calibration curves between the dissolved PCB concentration and the mass measured on the SPME fibre were developed, and the variability of this method was examined. We measured the uptake (k_1) and release (k_2) rate constants for this method and calculated K_{SPME} equilibrium values. Experiments were also conducted to examine any potential matrix effects that might occur because of particles and dissolved organic carbon present in natural waters. Dissolved PCB concentrations measured using this new SPME technique were compared with measurements made by traditional XAD resin extraction of natural waters.

2. Experimental

2.1 *SPME fibres*

Optical cable (Fiberguide Industry, Stirling, NJ) consisted of a 210 μm-diameter glass core and a 10 μm-thick PDMS coating. The volume of the PDMS coating was 6.6 μL of PMDS per metre of fibre. The cable came with a Nylon cladding 20 μm thick that covered the PDMS coating. The fibres used in this study were obtained from the same

source as used and evaluated in previous studies [23]. To make the SPME fibres, the cable was cut into 7.1 cm sections, and the Nylon cladding was removed from the bottom 8 mm, according to the manufacturer's directions, by dipping one end of the fibre for 20 s into propylene glycol heated to 82°C. After heating, any remaining Nylon was wiped away. The fibres were further conditioned by soaking in methanol for 10 min and rinsing with deionized (DI) water prior to use. For injection into the GC, a 5 mm silicone rubber septum (Supelco, Bellefonte, PA) was attached to the top of the SPME fibre and then inserted into a 22-gauge Rheodyne needle. Prior to inserting the SPME fibre into the needle, an 11 mm flat disk septum (Agilent Technologies, Palo Alto, CA) was attached to the end of the needle. A tight seal formed between the two septa when the SPME fibre was injected into the GC. In this design, only 8 mm of the fibre is inserted into the GC (figure 1).

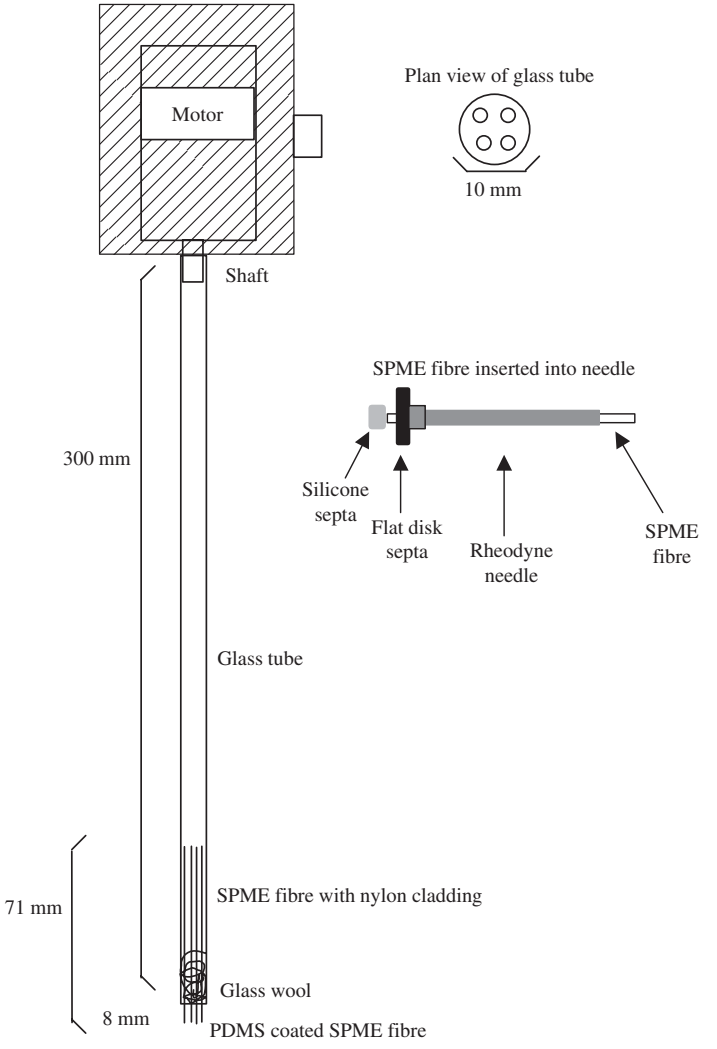

Figure 1. Schematic of the revolving SPME apparatus.

2.2 *Standards*

An Aroclor 1248 standard in hexane purchased from Ultra Scientific (North Kingston, RI) is a mixture of various PCB congeners. The mixture was diluted with hexane to a concentration of 2 μg total PCB mL^{-1}. The dominant PCBs in this mixture are tri- and tetra-chlorinated congeners [24]. Results presented in this article will focus on the major PCB congeners in the Aroclor 1248 mixture (those >2% by weight) i.e. PCB IUPAC congener number 18, 17, 31, and 28 (unresolved), 52, 49, 44, 74, 70, 66, 95, 101, 110, and 77 (unresolved), and 118.

2.3 *Gas chromatography*

The fibres were analysed using cool on-column injection into an Agilent model 6890 GC equipped with a ^{63}Ni electron capture detector (GC-ECD). Hydrogen was the carrier gas, and nitrogen was the make-up gas. The column was a 30 m DB-5 with a stationary phase thickness of 250 μm attached to a guard column with an internal diameter of 520 μm. The inlet temperature was held at 100°C until the fibre was inserted into the column. After insertion, the temperature in the injection port rose at 350°C min^{-1} until it reached a final temperature of 290°C in 50 s. The fibre was held at the head of the column for 1.5 min. The oven was held at initial temperature of 70°C for 2 min, then heated at a rate of 12°C min^{-1} to 140°C, 2.5°C min^{-1} to 230°C, and 10°C min^{-1} to 300°C where it was maintained for 1 min. The total run time was 51.82 min.

2.4 *Revolving SPME apparatus*

In order to utilize SPME fibres in natural waters, the thickness of the unstirred water layer needs to be minimized and reproducibly controlled. A motor (Tamiya Inc., Shizuka, Japan) powered by two AA batteries was configured to spin a shaft at 130 rpm. Glass tubes 300 mm in length and 10 mm in diameter were attached to the shaft. One end of the tube was sealed, and four holes <1 mm in diameter were punched in the end of it. Glass wool was then inserted down the barrel of the tube to hold the SPME fibres in place. One SPME fibre was inserted into each hole such that 8 mm of PDMS coated fibre extended from the end of the tube (figure 1), allowing collection of pseudo-replicate samples. The glass tube with the four SPME fibres on its end was easily attached or detached from the motor for sampling. In this method of sampling, the SPME fibres revolve in the water, and the sampling device can be directly deployed in surface waters. All other uses of non-equilibrium SPME involve stirring or agitating the water in a sample container while holding the SPME fibre still [7–11, 13].

2.5 *Spiked water calibration*

Standard water solutions containing Aroclor 1248 were made to calibrate the rate at which each congener mass accumulated on the revolving SPME fibre. Five solutions of Aroclor 1248 were prepared in clean 4 L glass bottles. Various amounts of Aroclor 1248 were placed in a syringe and slowly dripped into the empty bottles. The hexane was allowed to evaporate, and the vials were then completely filled with DI water. Five concentrations of Aroclor 1248 were prepared, containing 0, 0.25, 0.5, 1,

and 2 μg L^{-1} of total PCBs, respectively. The bottles were equilibrated for seven days at 25°C before they were analysed. Water from each bottle was analysed using SPME and our laboratory's standard liquid/liquid extraction procedure [25]. The solubility of the PCB congeners examined ranged from 0.04 to 2.0 mg L^{-1} [26], and the concentration of each PCB congener in DI water was well below the solubility limit.

2.6 *Matrix interference evaluation*

To test for matrix interferences when using the revolving SPME technique, dissolved PCB solutions were prepared by equilibrating known gas-phase PCB concentrations with DI water and more complex aqueous solutions/suspensions. The procedure to generate dissolved PCB concentrations is described in detail by Kucklick *et al.* [27] and briefly summarized here. Gas-phase generator columns were prepared as follows: neat PCB congeners (Ultra Scientific, North Kingston, RI) were dissolved in methylene chloride. Chromosorb W beads (Alltech, Deerfield, IL) were cleaned in an oven at 232°C for 4 h prior to use. The PCB solutions were poured over the Chromosorb beads, slowly evaporated, and the PCB-coated Chromosorb poured into a generator column. Air flowing through the generator columns became saturated with PCBs, and this air was diluted with clean humidified air and bubbled through 150 mL of DI water. The time to equilibrium was established by trapping air exiting the bubbler on polyurethane foam adsorbents (PUF). Analysis of multiple PUFs showed that equilibrium was established in 3 days. Once equilibrium was reached, the bubbling was shut off, and SPME was used to measure the dissolved PCB concentration.

Dissolved organic carbon (DOC)-enriched water was collected from Battle Creek Cypress Swamp located in Calvert County, Maryland, USA. This water was filtered through a 47 mm Whatman glass fibre filter (0.7 μm pore size) to remove suspended solids and placed into a bubbler. The DOC concentration of the filtered water was 8 mg L^{-1}. PCB saturated air was bubbled through 150 mL of this filtered water and allowed to come to equilibrium. Once equilibrium was reached, the gas was shut off, and SPME was used to measure the dissolved PCB concentration. Sediment was collected from Fishing Bay, an embayment of the Chesapeake Bay. Dry sediment was added to deionized water for a total suspended solids concentration of 200 mg L^{-1}. PCB saturated air was bubbled through 150 mL of this suspension until it came to equilibrium. Once equilibrium was reached, the bubbling was shut off, and SPME was used to measure the dissolved PCB concentration. While the DOC and sediment added to the bubblers might have contained PCBs such that the total PCB concentration was higher in those bubblers than in that containing only DI water, the dissolved phase concentration in the bubblers was controlled by equilibrating with PCB contaminated air.

2.7 *XAD comparison*

To compare this revolving SPME technique to the more traditional dissolved phase PCB measurements made by XAD extraction, 12 contaminated water samples were first analysed by SPME, and then the water was filtered and pumped through an XAD column. The PCB contaminated water was collected in 18 L stainless steel

tanks as part of another ongoing study in our laboratory [28]. The stainless steel tanks were shaken, and then the SPME fibres were deployed in the tanks for 30 min. After SPME deployment, the dissolved and particulate phase were separated by pumping the water through a glass-fibre filter (Schleicher and Schuell, Keene, NH; No. 25; 0.7 μm pore size) and an Amberlite XAD-2 macroresin (Sigma Aldrich, St Louis, MO). The XAD analysis followed the standard protocol of our laboratory and is briefly summarized here [3]. The samples were spiked with PCB surrogate standards 3,5-dichlorobiphenyl (IUPAC #14), 2,3,5,6-tetrachlorobiphenyl (IUPAC #65), and 2,3,4,4′,5,6-hexachlorobiphenyl (IUPAC #166) and Soxhlet extracted for 24 h in 1 : 1 acetone/hexane. Following a liquid/liquid extraction of the acetone/hexane mixture using DI water and hexane, the samples were concentrated to 1 mL, and eluted through a Florisil column (60–100 mesh; J.T. Baker Co., Phillipsburg, NJ). The purified extracts were concentrated and analysed using a Hewlett-Packard 5890 gas chromatograph with a 60 m DB-5 column and a ^{63}Ni electron capture detector (GC-ECD). Each sample was analysed for 55 individual PCB congeners and 28 chromatographically unresolved congener groups. Internal standards consisting of 2,3,6-trichlorobiphenyl (IUPAC #30) and 2,2′3,4,4′,5,6,6′-octachlorobiphenyl (IUPAC #204) were added to each sample prior to instrumental analysis to calculate relative response factors for each congener. Each PCB congener was identified based on its retention time relative to a standard mixture of PCB Aroclors 1232, 1248, and 1262 (Ultra Scientific, Kingston, RI).

3. Results and discussion

3.1 *Analytical verification of GC technique*

Prior to conducting experiments, tests were run to verify the consistency of the SPME fibres and the precision of the GC injections. Ten nanograms of Aroclor 1248 were dripped onto the end of a fibre which was analysed on the GC. This procedure was repeated 10 times using new fibres for each repetition. The detector responses of each congeners were compared to determine the precision of this method. The relative standard deviation (RSD) ranged from 2.3 to 7.6% for all congeners, and there was no trend in RSD with PCB solubility or K_{ow}. These results are similar to the precision of head space SPME analysis for various PCB congeners [14].

Even though these SPME fibres are designed to be disposable, carryover after one use was examined to analyse the efficiency of desorption in the injection port. To do this analysis, 10 ng of Aroclor 1248 was added to an SPME fibre and analysed. After this first run was completed, the fibre was re-injected into the GC. Carryover was less than 1% for all congeners examined, indicating that this method of analysis had a desorption efficiency of over 99%. Landin *et al.* [14] also found no significant carryover of PCB congeners when commercially available SPME fibres (Supelco, Bellefonte, PA) were injected into a GC/MS/MS system. However, other studies examining the carryover of PCB congeners have found carryover rates as high as 25% [10, 16]. A variety of conditions contribute to the wide range of carryover rates observed in the literature, including the amount of time the fibre is held in the GC and temperature of desorption.

In the method described in this paper, SPME fibres were not reused, and carryover between GC runs was therefore not an issue.

Since SPME injections into the GC are done manually, it is desirable to store the fibres in the freezer before analysis. However, some studies suggest that PCBs might volatilize or become irreversibly bound to the SPME fibres during storage. Lighter, more volatile compounds are especially prone to loss if not stored properly [29, 30]. To examine the loss of PCBs during freezing, 10 ng of Aroclor 1248 was dripped on several SPME fibres, and the fibres were frozen inside a glass capillary tube for 30 days. There was no significant difference in the detector response between stored fibres and freshly prepared fibres ($p > 0.05$, $n = 5$). PCBs were not lost during storage, and no additional unknown contaminant peaks were detected on the SPME fibres as a result of storage.

3.2 *Method precision*

In order to examine the precision of the revolving-fibre technique, multiple samples were collected from various concentrations of dissolved PCBs. The variation in detector response among the four SPME fibres on a single rotating glass tube was compared with the variation among different glass tubes. SPME fibres deployed in all of the calibration solutions for 30 min showed similar variability, and the between-tube RSD for all of the calibration points ranged from 3.0 to 18.9%, which did not vary with concentration. The RSD of the four SPME fibres on the same glass tube was similar to the between-tube relative standard deviation and ranged from 3.2 to 16.7% in the $5\,\mu g\,L^{-1}$ PCB solution. This suggests that there is no sampling bias among the different positions on the rod and that PCBs partition into all the fibres on a glass tube at the same rate. There was no trend in RSD with PCB solubility or K_{ow}, and the method is not biased toward better reproducibility for the congeners with lower K_{ow} values. These results are consistent with the 5–26% RDS values reported in the literature for other non-equilibrium SPME techniques [10, 16].

3.3 *Kinetics of PCB uptake*

The goal of developing a non-equilibrium technique was to measure individual PCBs in the dissolved phase with suitable detection limits in 30 min. In order to examine the uptake of PCBs into the revolving fibres, they were exposed for various lengths of time, ranging from 5 min to 12 h, in a 4 L bottle spiked with $5\,\mu g\,L^{-1}$ of Aroclor 1248 in DI water (figure 2). A detailed analysis of the uptake of PCBs onto the fibre during exposure times ranging from 5 to 120 min was conducted. During this time period, there was negligible depletion of the dissolved phase, and a linear relationship between mass extracted and SPME sampling time was observed. The correlation coefficient ranged from 0.88 to 0.98 for various PCB congeners (figure 2). For all PCB congeners examined, the 30 min sampling period fell well within the linear range of uptake onto the SPME fibres, indicating that it was a suitable exposure time to use with our method (figure 2). The linear relationship suggests that diffusion through the UWL was the rate-limiting uptake step, since longer exposure times resulted in more mass accumulating on the SPME fibre. The slope of the line represents a mass uptake rate, which ranged from 0.2 to $2.2\,pg\,min^{-1}$ for the various congeners. The rate of uptake

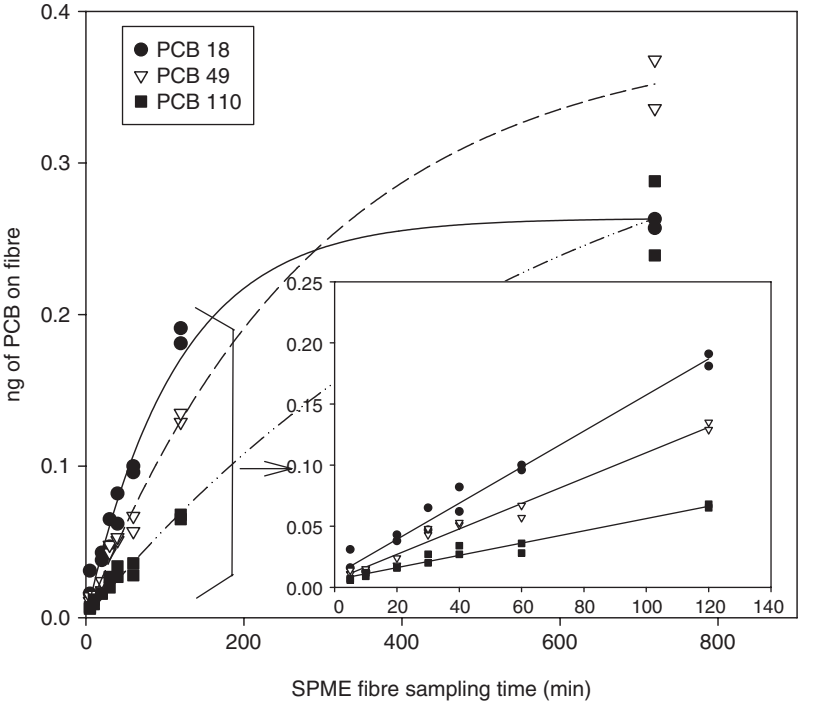

Figure 2. Uptake curves of selected PCBs onto the SPME fibres deployed in DI water spiked with $5\,\mu g\,L^{-1}$ of Aroclor 1248. The SPME fibres sampled the water continuously for time periods ranging from 5 min to 12 h at 25°C. For clarity, only results from a few selected congeners are depicted. Multiple data points for a given time indicate pseudo-replicate measurements.

of PCBs onto the SPME fibres was positively correlated with the molecular diffusion coefficient in water ($r^2 = 0.51$), further indicating that diffusion through the UWL was the limiting step in the uptake process. The rate of diffusion of PCBs into the PDMS coating is controlled by diffusion through the UWL if the thickness of the UWL is greater than the thickness of the PDMS coating divided by K_{SPME} [31]. For PCBs, K_{SPME} ranges from 10^5 to 10^6, and diffusion through the UWL is almost always the rate-limiting step.

Since the utility of this SPME technique depends on short sampling periods, longer fibre exposure times were not examined in great detail. Nevertheless, it is useful to calculate rate constants for our sampling technique in order to compare our results to literature values. Uptake and elimination rate constants were determined by curve-fitting the model (equation 3) to our data. For this method, the uptake rate constant (k_1) ranged from 350 ± 100 to $950 \pm 170\,min^{-1}$, the elimination rate constant (k_2) ranged between 0.0023 ± 0.0002 and $0.0089 \pm 0.0006\,min^{-1}$, and log K_{SPME} ranged from 4.96 to 5.31 (table 1, $n = 4$).

There are only a limited number of studies examining the kinetics of PCB uptake onto SPME fibres in the literature. Oomen *et al.* [20] vibrated 1-mm-long fibres in PCB-spiked water using the Varian 8200 CX autosampler. In that study, PCB 52 had an uptake rate constant of $6700 \pm 1200\,min^{-1}$ and an elimination rate constant of $0.014 \pm 0.003\,min^{-1}$; and PCB 118 had uptake and elimination rate

Table 1. Kinetic constants for the uptake of PCBs onto the SPME fibres ($n = 4$).

IUPAC name	Congener number	k_1 (/min) ± SE	k_2 (/min) × 10^{-3} ± SE	Log K_{SPME} ± SE
2,2′,5-Trichlorobiphenyl	18	810 ± 100	8.9 ± 0.6	4.96 ± 0.05
2,2′,4-Trichlorobiphenyl	17	430 ± 60	6.0 ± 0.7	4.85 ± 0.05
2,4′,5 and 2,4,4′-trichlorobiphenyl	31, 28	650 ± 90	6.0 ± 0.8	5.04 ± 0.05
2,2′,4,6′-Tetrachlorobiphenyl	52	700 ± 60	3.0 ± 0.2	5.37 ± 0.05
2,2′,4,5′-Tetrachlorobiphenyl	49	950 ± 170	5.0 ± 0.8	5.28 ± 0.05
2,2′,3,5′-Tetrachlorobiphenyl	44	800 ± 150	4.3 ± 0.7	5.27 ± 0.06
2,4,4′,5-Tetrachlorobiphenyl	74	720 ± 190	3.6 ± 0.8	5.30 ± 0.06
2,3′,4′,5-Tetrachlorobiphenyl	70	480 ± 50	2.3 ± 0.2	5.32 ± 0.05
2,3′,4,4′-Tetrachlorobiphenyl and 2,2′,3,5′,6-pentachlorobiphenyl	66, 95	800 ± 160	4.2 ± 0.7	5.28 ± 0.06
2,2′,4,5,5′-Pentachlorobiphenyl	101	720 ± 190	3.6 ± 0.8	5.30 ± 0.06
2,3,3′,4′,6-Pentachlorobiphenyl	110	740 ± 190	3.6 ± 0.8	5.31 ± 0.06
2,3′,4,4′,5-Pentachlorobiphenyl	118	350 ± 100	3.5 ± 0.9	5.00 ± 0.07

constants of 9600 ± 1200 and $0.017 \pm 0.003\,\text{min}^{-1}$, respectively. Ramos *et al.* [21] measured the uptake of dissolved PCB 77 in a solution that was stirred at a rate of 1000 rpm and calculated a k_1 value of $1530 \pm 170\,\text{min}^{-1}$ and a k_2 value of $0.025 \pm 0.004\,\text{min}^{-1}$. The literature values of k_1 and k_2 are an order of magnitude higher than those found in this study. The uptake (k_1) and elimination (k_2) rate constant depend on the specific technique used to vibrate or shake the fibres in the sample. In these studies, the SPME fibre was vibrated more vigorously than in our study, resulting in a thinner UWL and greater uptake and elimination rate constants. Since mass accumulation onto a SPME fibre depends on diffusion through the UWL, different techniques will result in different uptake and elimination rate constants.

Studies such as those conducted by Baltussen *et al.* [32] and Mayer *et al.* [9] found a linear relationship between the K_{SPME} and K_{ow}. This relationship was not observed in our SPME technique; however, our values are within the range of K_{SPME} values reported in the literature. For example, the log K_{SPME} of PCB 52 calculated in this study (5.37) agreed well with those measured by Meyer *et al.* (5.37 [9]), Poerschmann *et al.* (5.31 [8]), Baltussen *et al.* (5.11–5.44 depending on the amount of PDMS coated to fused silica beads [32]), and calculated by Oomen *et al.* (5.7 [20]). For PCB congener 118, Poerschmann *et al.* [8] measured a log K_{SPME} of 5.60; this study found a log K_{SPME} of 5.0, and Meyer *et al.* [9] measured a log K_{SPME} value of 5.9. In Poerschmann *et al.* [8] and Baltussen *et al.* [32], K_{SPME} was calculated as C_{PDMS}/C_{water}, in this study, and in the Oomen *et al.* study [20], K_{SPME} was calculated as k_1/k_2.

3.4 *Dissolved phase calibration*

To correlate the mass on the SPME fibre to actual dissolved concentrations, the revolving SPME fibres were deployed for 30 min in solutions of DI water spiked with 0, 0.25, 0.5, 1, and $2\,\mu\text{g L}^{-1}$ of Aroclor 1248. After SPME fibre deployment, a liquid/liquid extraction of the water was conducted using our laboratory's standard extraction procedure. For each PCB congener, the mass measured on the SPME fibre

Table 2. Regression statistics for the relationship between dissolved PCB concentrations and mass measured on the SPME fibre after 30 min of exposure ($n = 4$).

Congener number	Slope ± SE (mL)	Coefficient of determination (r^2)	MDL (ng L^{-1})
18	0.57 ± 0.01	0.91	1.9
17	0.71 ± 0.01	0.95	0.6
31, 28	0.50 ± 0.06	0.96	5.2
52	0.68 ± 0.06	0.97	3.5
49	0.68 ± 0.07	0.97	2.2
44	0.55 ± 0.09	0.92	5.3
74	0.50 ± 0.03	0.99	0.9
70	0.38 ± 0.05	0.97	2.0
66, 95	0.58 ± 0.04	0.99	2.6
101	0.66 ± 0.06	0.98	0.2
110	0.41 ± 0.03	0.99	0.7
118	0.29 ± 0.03	0.98	1.9

was correlated to dissolved phase concentration measured by liquid/liquid extraction. For all PCB congeners, uptake onto the SPME fibres was linear over the range of dissolved concentrations examined with coefficients of determination ranging from 0.91 to 0.99 (table 2). These strong linear relationships demonstrate that the measured mass on the SPME fibre was directly related to the dissolved concentration. At the highest Aroclor concentration examined, the concentration of each PCB congener in the PDMS fibre was less than 0.01 g L^{-1} PDMS. No relationship was observed between uptake onto the SPME fibre and PCB properties such as molecular weight. However, only tri, tetra, and penta-chlorinated congeners were examined in this study.

3.5 *Detection limits*

The method detection limit (MDL) was defined as three times the average mass in the deionized water blank samples. This mass was then converted to concentration using the calculated calibration curves. The MDL for the congeners examined in this study ranged from 0.6 to 5.2 ng L^{-1} (table 2). For all congeners, the MDL was below the lowest concentration sampled in the calibration curve. Other studies using SPME report PCB detection limits ranging from 2 to 20 ng L^{-1}, similar to results obtain in this study [10, 16, 33].

3.6 *Matrix effects*

In order to use this revolving SPME technique to measure PCBs in natural waters, other matrices present in the water, such as dissolved organic carbon, could not interfere with the uptake of PCBs onto the fibres. The bubbler system maintained constant dissolved PCB concentrations and was designed to test for matrix interferences with this SPME technique. For various PCB congeners, the dissolved PCB measurements made in DI water were not significantly different from the dissolved measurements made in the presence of DOC or suspended solids (figure 3, $p > 0.05$ for all congeners, $n = 6$). This result indicates that the revolving SPME technique is suitable to measure PCBs in natural waters, and the presence of matrices does not influence

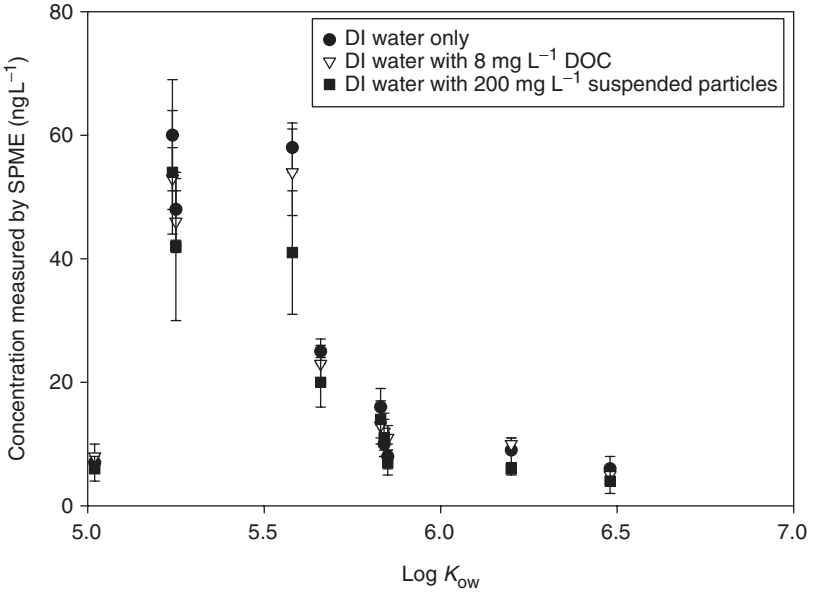

Figure 3. SPME measurements of the dissolved concentrations of PCB congeners measured in DI water, DI water plus DOC, and DI water plus suspended solids. The error bars represent the standard deviation between pseudo-replications and multiple tube measurements ($n = 6$).

the uptake of dissolved PCBs onto the SPME fibres. This finding confirms results found by other researchers for both the equilibrium [13, 22] and non-equilibrium techniques [15, 20, 21]. For example, Ramos *et al.* [21] prepared two solutions of dissolved PCB 77; one contained 20 mg L^{-1} humic acid, and the other did not. An air bridge connected the round bottom flasks containing the two solutions. The authors found no significant difference in the detector response to SPME fibre measurements made in both flasks, indicating that humic acid did not interfere with the uptake of PCBs onto SPME fibre.

3.7 *XAD/SPME comparison*

The revolving SPME technique was used to sample well water that was mixed with PCB contaminated sediment from the Hudson River [28]. After the revolving SPME fibres were deployed in the water for 30 min, the water was pumped first through a glass-fibre filter to remove particles and then an XAD column to measure the dissolved phase. A total of 12 XAD/SPME pairs were analysed and compared. Information in the literature suggests that PCB concentrations measured by XAD should be higher than those measured by SPME because XAD measurements typically include PCBs bound to DOC [34], and SPME measurements do not. Results from this study confirm this hypothesis; dissolved PCB concentrations measured by SPME were slightly lower than dissolved concentrations measured by XAD (figure 4), even though the DOC concentration in the water was only 1.32 ± 0.23 mg L^{-1}. On average, the XAD measurements were 12% higher than the SPME measurements (figure 5). These results are consistent with the study by Zheng *et al.* [35] who found that SPME fibres deployed

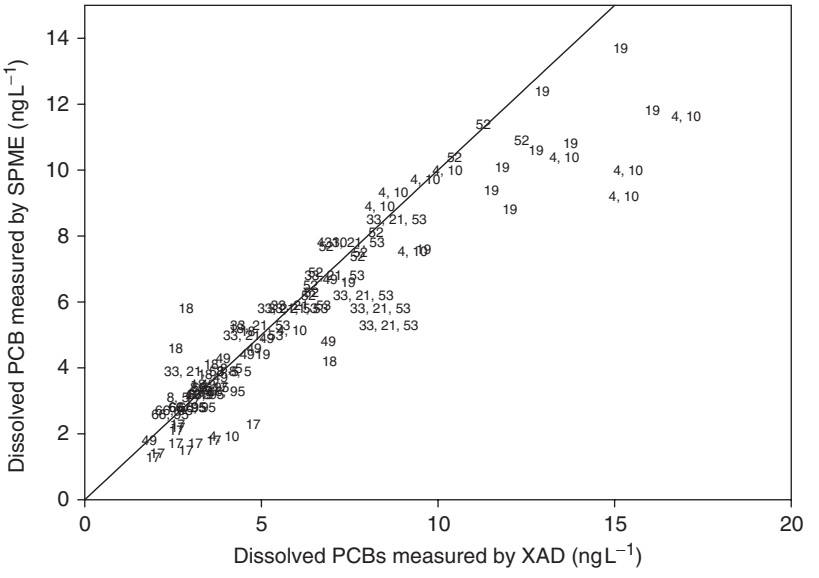

Figure 4. Comparison of dissolved PCB concentrations measured by the revolving SPME technique to measurements made by traditional XAD extraction. The line on the graph is the 1 : 1 line, and the numbers on the graph are the IUPAC PCB congener numbers.

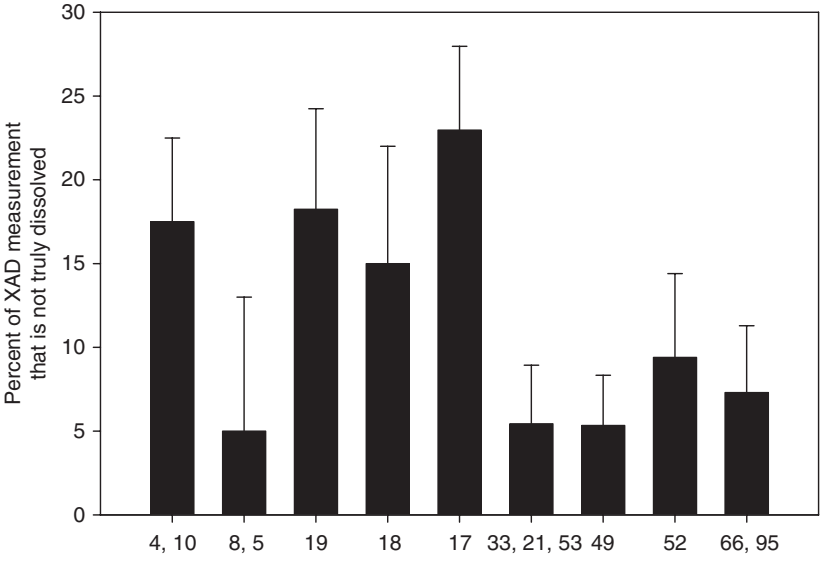

Figure 5. Average percentage difference between XAD and SPME measurements for each PCB congener. Congener 110 was not detected by this SPME technique, and XAD measurements indicate that the concentration was $\sim$0.5 ng L^{-1}, below the SPME detection limit.

as passive samplers measured DDE concentrations that were not statistically different from XAD extractions. The relationship between the XAD and SPME measurements strongly suggests that this revolving SPME technique is suitable for measuring PCB concentrations in the field.

4. Summary

This technique rapidly measures dissolved PCB congeners in natural waters in 30 min with detection limits ranging from 0.6 to 5.2 ng L^{-1}. Revolving the SPME fibres at 130 rpm rather than agitating the water reproducibly minimizes the thickness of the UWL and allows sufficient mass to diffuse onto the SPME fibres for reasonable detection limits. The mass that accumulates on the fibre is linearly related to the dissolved concentration, and the presence of both DOC and suspended solids does not interfere with the dissolved measurements made using this technique. The relative standard deviation between replicate SPME samples ranges from 3 to 20%. A comparison with XAD extraction of natural water shows that this SPME technique reliably and consistently measures dissolved PCB concentrations in natural waters.

Current field applications of SPME are best suited for time-weighted average measurements because the commercially available devices are essentially passive samplers [30]. This revolving SPME technique can be used on shorter timescales to less expensively and more rapidly monitor short-term variability in dissolved concentrations of contaminants. Pseudo-replicate samples are easily collected to assess analytical variability. Although this technique requires manual injection, the fibres can be safely stored in the freezer until they are analysed. This type of SPME device can be made relatively cheaply by buying the SPME fibres from an optical fibre company and motors from a local hobby shop; it eliminates the need for expensive lab equipment to conduct SPME analysis and provides a more economical way to conduct field studies. However, given the high detection limits of this technique, it is currently most useful for sampling experimental systems or highly contaminated sites, provided that potentially interfering co-contaminants are evaluated. Further research to increase the sensitivity of this technique would need to be conducted in order to sample ambient surface waters.

Acknowledgements

We thank the Hudson River Foundation, Inc. and the Maryland Sea Grant REU program for providing support for this research. This is the University of Maryland Center for Environmental Science contribution number 3955.

References

[1] D.M. DiToro, C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, P.R. Paquin. *Environ. Toxicol. Chem.*, **10**, 1541 (1991).
[2] L.A. Totten, P.A. Brunciak, C.L. Gigliotti, J. Dachs, T.R. Glenn, E.D. Nelson, S.J. Eisenreich. *Environ. Sci. Technol.*, **35**, 3834 (2001).
[3] H.A. Bamford, F.C. Ko, J.E. Baker. *Environ. Sci. Technol.*, **36**, 4245 (2002).
[4] J.N. Huckins, M.W. Tubergen, G.K. Manuweera. *Chemosphere*, **20**, 533 (1990).
[5] J.N. Huckins, G.K. Manuweera, J.D. Petty, D. Mackay, J.A. Lebo. *Environ. Sci. Technol.*, **27**, 2489 (1993).
[6] A.L. Rantalainen, W.J. Cretney, M.G. Ikonomou. *Chemosphere*, **40**, 147 (2000).

[7] C.L. Arthur, J. Pawliszyn. *Anal. Chem.*, **62**, 2145 (1990).
[8] J. Poerschmann, T. Gorecki, F.D. Kopinke. *Environ. Sci. Technol.*, **34**, 3824 (2000).
[9] P. Mayer, W.H.J. Vaes, J.L.M. Hermens. *Anal. Chem.*, **72**, 459 (2000).
[10] Y. Yang, D.J. Miller, S.B. Hawthorne. *J. Chromatogr.*, **800**, 257 (1998).
[11] J. Pawliszyn. In *Applications of Solid Phase Microextraction*, J. Pawliszyn (Ed.), pp. 3–21, Royal Society of Chemistry, Cambridge (1999).
[12] B. Zygmunt, A. Jastrzebska, J. Namiesnik. *Crit. Rev. Anal. Chem.*, **31**, 1 (2001).
[13] J. Poerschmann, F.D. Kopinke, J. Pawliszyn. *J. Chromatogr.*, **816**, 159 (1998).
[14] P. Landin, M. Llompart, M. Lourido, R. Cela. *J. Microcolumn Sep.*, **13**, 275 (2001).
[15] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller. *Anal. Chem.*, **68**, 144 (1996).
[16] D.W. Potter, J. Pawliszyn. *Environ. Sci. Technol.*, **28**, 298 (1994).
[17] V.V. Cardoso, A. Rodrigues, J. Correia, M.J. Benoliel. *Polycycl. Aromat. Comp.*, **19**, 227 (2000).
[18] M. Llompart, K. Li, M. Fingas. *Anal. Chem.*, **70**, 2510 (1998).
[19] W.H.J. Vaes, E.U. Ramos, H.J.M. Verhaar, W. Seinen, J.L.M. Hermens. *Anal. Chem.*, **68**, 4463 (1996).
[20] A.G. Oomen, P. Mayer, J. Tolls. *Anal. Chem.*, **72**, 2802 (2000).
[21] E.U. Ramos, S.N. Meijer, W.H.J. Vaes, H.J.M. Verhaar, J.L.M. Hermens. *Environ. Sci. Technol.*, **32**, 3430 (1998).
[22] F.D. Kopinke, J. Poerschmann, A. Georgi. In *Applications of Solid Phase Microextraction*, J. Pawliszyn (Ed.), pp. 111–128, Royal Society of Chemistry, Cambridge (1999).
[23] P. Mayer, W.H.J. Vaes, F. Wijnker, K. Legierse, R.H. Kraaij, J. Tolls, J.L.M. Hermens. *Environ. Sci. Technol.*, **34**, 5177 (2000).
[24] G.M. Frame, J.W. Cochran, S.S. Bowadt. *HRC-J. High Res. Chrom.*, **19**, 657 (1996).
[25] H.A. Bamford, J.H. Offenberg, R.K. Larsen, F.C. Ko, J.E. Baker. *Environ. Sci. Technol.*, **33**, 2138 (1999).
[26] W.Y. Shiu, K.C. Ma. *J. Phys. Chem. Ref.*, **29**, 387 (2000).
[27] J.R. Kucklick, D.A. Hinckley, T.F. Bidleman. *Mar. Chem.*, **34**, 197 (1991).
[28] A.R. Schneider, E.T. Porter, J.E. Baker. *Abstr. Pap. Am. Chem. Soc.*, **225**, U839 (2003).
[29] M. Chai, J. Pawliszyn. *Environ. Sci. Technol.*, **29**, 693 (1995).
[30] L. Muller. In *Applications of Solid Phase Microextraction*, J. Pawliszyn (Ed.), pp. 269–283, Royal Society of Chemistry, Cambridge (1999).
[31] J. Pawliszyn. *Solid Phase Microextraction Theory and Practice*, pp. 58–67, Wiley-VCH, New York (1997).
[32] E. Baltussen, P. Sandra, F. David, H.G. Janssen, C. Cramers. *Anal. Chem.*, **71**, 5213 (1999).
[33] E. Martinez, P. Landin, A.M. Carro, M.P. Llompart, R. Cela. *J. Environ. Monitor.*, **4**, 490 (2002).
[34] S. Lee, J. Gan, W.P. Liu, M.A. Anderson. *Environ. Sci. Technol.*, **37**, 5597 (2003).
[35] E.Y. Zeng, D. Tsukada, D.W. Diehl. *Environ. Sci. Technol.*, **38**, 5737 (2004).