JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Determination of Enantiomers of Synthetic Pyrethroids in Water by Solid Phase Microextraction − Enantioselective Gas Chromatography

WEIPING LIU AND JAY J. GAN*

Department of Environmental Sciences, University of California, Riverside, California 92521

Solid phase microextraction (SPME) is an ideal sample preparation technique because of its speed and solvent-free features. Sampling by SPME is selective and only the dissolved concentration is measured, which allows measurement of the bioavailable fraction of a contaminant in aqueous media. One potential application of SPME is for analysis of enantiomers of chiral contaminants in environmental samples. In this study, a method was developed for determining enantiomers of (*Z*)-*cis*-bifenthrin and *cis*-permethrin in water using coupled SPME and enantioselective gas chromatography (GC). Following SPME sampling, enantiomers of (*Z*)-*cis*-bifenthrin and *cis*-permethrin were separated at the baseline on a β-cyclodextrin-based enantioselective column, and analyte enrichment onto the SPME fiber was not enantioselective. The GC response increased as sampling time was increased from 0 to 240 min, and as sampling temperature was increased from 20 to 40 °C. Organic solvents such as methanol, acetone, and acetonitrile enhanced, while soil extracts slightly decreased, the GC response. The integrated SPME-enantioselective GC method was used to analyze surface runoff samples. The analysis showed preferential degradation of the 1*S*-3*S* enantiomer over the 1*R*-3*R* enantiomer for both (*Z*)-*cis*-bifenthrin and *cis*-permethrin. The concentrations detected by SPME-GC were substantially smaller than those determined following solvent extraction, suggesting that SPME-enantioselective GC analysis selectively measured the dissolved fraction.

KEYWORDS: Solid-phase microextraction; SPME; chiral analysis; enantiomer separation; synthetic pyrethroids; enantioselective analysis

INTRODUCTION

Many methods for the determination of pesticides or other organic compounds in water involve liquid−liquid extraction (LLE) for sample preparation, followed by chromatographic detection. Although LLE has wide applications, it requires large amounts of organic solvents and is usually time and labor-consuming. Solid phase microextraction (SPME) is an extraction technique that was first developed in the early 1990s by Pawliszyn and colleagues (*1*) and has been used increasingly over the past decade. A great number of applications have been reported for SPME for extracting organic compounds, including a wide variety of pesticides, from water samples (*2*−*5*). In SPME sampling, polymer-coated fibers are used to enrich target analytes directly from the aqueous phase or from the headspace above an aqueous sample (*1*). When coupled with GC analysis, the enriched SPME fiber is transferred directly to the GC inlet where the analyte is thermally desorbed and eluted on a GC column. Compared to traditional LLE methods, coupled SPME-GC analysis is solvent-free, and when optimized, provides excellent reproducibility and sensitivity (*2*−*5*). Another significant advantage of SPME sampling is its ability to allow selective detection of the freely dissolved form of an analyte in aqueous media containing suspended solids or dissolved organic matter (DOM). This feature allows measurement of the bioavailable concentration of the contaminant (*6*−*9*). In contrast, LLE does not distinguish the sorbed and dissolved phases, and the measured concentration cannot be correlated with bioavailability. Previous studies showed that for strongly sorbing compounds such as synthetic pyrethroids, nonselective analysis may lead to significant overestimation of aquatic toxicity for runoff or surface water samples (*9*).

Many environmental contaminants are chiral compounds containing multiple enantiomers (*10*−*12*). Enantiomers of a compound are known to have identical physical and chemical properties but often different biological properties (*10*, *12*). In the environment, enantiomers are known to be selectively degraded by microorganisms, resulting in different attenuation patterns or bioaccumulation potentials for enantiomers from the same compound (*10*, *12*−*16*). Therefore, analytical methods capable of detecting enantiomers will be of great value in future environmental monitoring. It is known that certain solvents can cause isomerization and thus alter the original isomer composition (*17*). SPME, because it is solvent-free, may thus offer a unique advantage over LLE and other solvent-based extraction techniques by preserving sample integrity. However, although there are many uses of SPME for determining residues of organochlorine (*18*, *19*), organophosphate (*4*), and synthetic

* To whom correspondence should be addressed. E-mail: jgan@mail.ucr.edu.

10.1021/jf035276f CCC: $27.50
Published on Web 01/20/2004

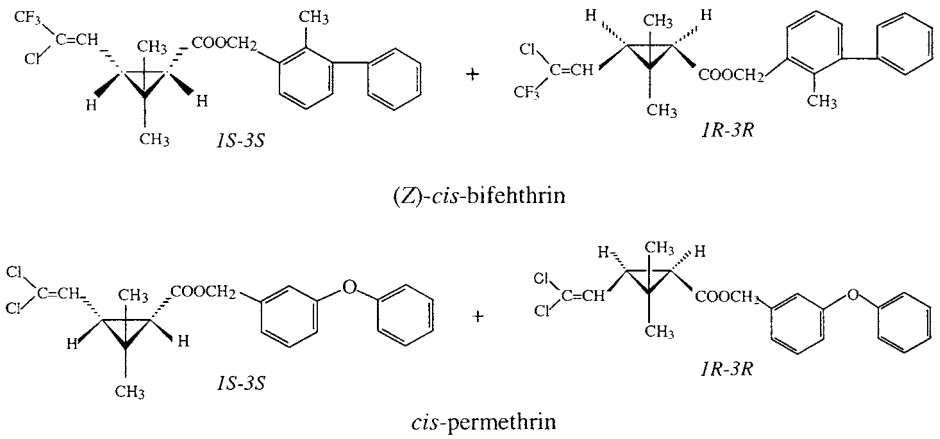

Figure 1. Enantiomer pairs of (**a**) (*Z*)-*cis*-bifenthrin and (**b**) *cis*-permethrin.

pyrethroid pesticides (*9, 20*), no application has been reported to date on its use for chiral analysis. In this study, we evaluated SPME for sampling enantiomers of synthetic pyrethroids (*Z*)-*cis*-bifenthrin (2-methylbiphenyl-3-ylmethyl (*Z*)−(1*RS*)-*cis*-3-(2-chloro-3,3,3- trifluoroprop-1-enyl)-2, 2-dimethylcyclopropanecarboxylate) and *cis*-permethrin (phenoxybenzyl (1*SR*)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate). Enantiomer enrichment was obtained with a poly(dimethylsiloxane) (PDMS) fiber, and isomer selectivity and effects of several SPME sampling variables were evaluated to achieve method optimization.

MATERIALS AND METHODS

Chemicals. Racemic standards of (*Z*)-*cis*-bifenthrin (*cis*-BF, purity >98.0%) and *cis*-permethrin (*cis*-PM, purity > 99.3%), and standard of enantiomer 1*R*-3*R*-BF (*RR*-BF, purity 97.2%) were all provided by FMC (Princeton, PA). The chemical structures of *cis*-BF and *cis*-PM are given in **Figure 1**. Stock solutions of *cis*-BF, *cis*-PM, and *RR*-BF were prepared in acetone at 1 mg mL^{-1} and stored at 4 °C before use. Other solvents and chemicals used in this study were of pesticide residue or analytical-reagent grade.

SPME Method Development. The SPME fiber (Supelco, Bellefonte, PA) used in this study was coated with a 100-μm layer of PDMS. Before its first use, the fiber was activated in the GC inlet at 260 °C for 30 min. The PDMS fiber was placed in a manual syringe assembly (Supelco) to facilitate sampling and sample introduction into GC. Working solutions of *cis*-BF, *cis*-PM, and *RR*-BF were prepared by diluting the stock solution with distilled water to obtain 100-mL aqueous solutions at concentrations specified below. A15-mL aliquot of the sample solution was transferred to a 20-mL glass scintillation vial, and the sample was stirred using a 2.0- × 7.0-mm magnetic bar at 600 rpm. Sampling was initiated when the SPME fiber was immersed into the sample solution 2.0 cm from the surface. After sampling for a given period of time, the SPME fiber was inserted in the GC inlet and exposed for 3.0 min, to cause thermal desorption of the enriched analyte. The inlet valve was closed for the first 1.0 min, to allow the desorbed analyte to enter the GC column.

To understand the dependence of the GC response on SPME sampling time, aqueous samples containing each enantiomer at 2.5 μg L^{-1} were prepared using *cis*-BF or *cis*-PM. The sampling time was incremented from 30 to 240 min, while the sampling temperature was kept at 20 ± 1 °C (room temperature). The dependence of the GC response on SPME sampling time was evaluated from the relationship of the GC signal output in area and sampling time. To evaluate the effect of sampling temperature on GC response, SPME sampling was carried out in aqueous samples equilibrated at 20, 25, 30, 35, or 40 °C. The concentration of each enantiomer was 1.5 μg L^{-1}, and the sampling time was kept at 60 min. The effect of temperature on method sensitivity was analyzed from the relationship between the GC signal output in area and temperature in °C. To determine the influence of cosolvents and other impurities in the sample media on SPME performance, aqueous solutions containing 5% methanol, acetone, acetonitrile, or a soil extract were fortified with *cis*-BF or *cis*-PM and used for SPME sampling. The soil extract was prepared by mixing a sandy loam soil with water at a 1:5 (w/w) ratio for 24 h and collecting the supernatant after centrifugation. Three replicates were used for each solvent or soil extract treatment. The sampling temperature was kept at 20 ± 1 °C (room temperature), and the sampling time was 60 min.

Method Evaluation. The tests described above were used to derive an optimized method, which was further evaluated for its sensitivity and linearity, and the feasibility for use with field samples. The method detection limit (MDL) was determined by analyzing a set of sequentially diluted solutions with known concentrations of *cis*-BF or *cis*-PM enantiomers. Three replicates were used for each concentration. The MDL was designated as 3 times the background noise of the instrument. Linear ranges were determined by applying the optimized method to the analysis of a series of aqueous solutions with known concentrations for each enantiomer. The linearity of the calibration curve was analyzed through linear regression of the GC signal output in area against concentration in μg L^{-1}. The upper (or lower) limit of the linear range was defined as the concentration point beyond which a curvature occurred along the fitted line.

The developed method was used to analyze a set of runoff samples taken from a runoff discharge channel at a nursery site located in Irvine, CA. Products of bifenthrin and permethrin had been used for over four years prior to the sampling date at the site. Runoff water was collected into 1-L glass bottles at six different locations along a 260-m paved channel and transported immediately to the laboratory for analysis. To determine the content of suspended solids in the runoff samples, a 200-mL aliquot was passed through a 5-cm glass fiber membrane with a pore size of 0.7 μm, and the change in membrane weight before and after filtration was measured. The runoff samples were subjected to extraction using two different methods as described below. In the first extraction method (LLE), a 200-mL aliquot was extracted with 30 mL of ethyl acetate in a 1-L glass separatory funnel by mixing for 1 min and collecting the solvent phase upon phase separation. The same extraction step was repeated for a total of three times, and the extracts were combined, dehydrated over sodium sulfate, condensed to 2.0 mL, and analyzed by GC using the conditions given below. In the second extraction method (SPME), a 15-ml aliquot was sampled for 60 min at room temperature, and the SPME fiber was analyzed by GC under the same conditions. Three replicates were used for each method on each sample.

GC Conditions. Enantioselective separation was achieved on a 30-m × 0.25-mm × 0.25-μm (film thickness) enantioselective capillary column BGB-172 (20% *tert*-butyldimethylsilyl-β-cyclodextrin dissolved in 15% diphenyl- and 85% dimethyl-polysiloxane; BGB Analytik, Adliswil, Switzerland). An Agilent 6890N GC equipped with an electron capture detector (ECD) was used for the detection of *cis*-BF and *cis*-PM enantiomers. The column flow rate was 1.5 mL min^{-1} (helium). The GC was operated in the splitless mode for the first 1.0 min, and the inlet temperature was 260 °C. The detector temperature was 310 °C, and makeup gas was N_2 (60 mL min^{-1}). The column temperature was programmed as follows: initial hold at 180 °C for 2

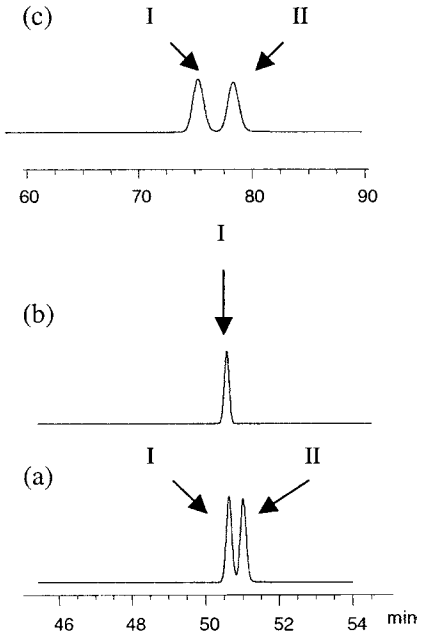

Figure 2. Chiral GC chromatograms of (**a**) (*Z*)-*cis*-bifenthrin, (**b**) *1R-3R*-bifenthrin and (**c**) *cis*-permethrin.

min, first ramp at 1 °C min^{-1} to 230 °C, and final hold at 230 °C until complete elution. The GC signal output was recorded as peak area.

RESULTS AND DISCUSSION

Separation of Enantiomers. While the commercial formulations of BF contain only *cis*-BF, those of PM typically contain both cis- and *trans*-PM. The enantiomer pair of *cis*-BF or *cis*-PM is 1*S*-3*S* and 1*R*-3*R* in **Figure 1**. Under the used conditions, baseline separation was achieved for enantiomers in both *cis*-BF and *cis*-PM, using the coupled SPME-enantioselective GC analysis (**Figure 2**). However, the *trans*-PM enantiomer pair was eluted as only one peak that had a retention time much longer than that for *cis*-PM enantiomers. Using alternate chiral columns including BETADTX-120 (Supelco), BGB-176 (Analytik) and HP Cyclosil-β (Agilent) did not improve the resolution of the *trans*-PM enantiomers. Therefore, *trans*-PM was not considered in this study. Elution of *cis*-BF on the enantioselective column gave two separated peaks with retention times of 50.2 min (I) and 50.9 min (II) under the conditions used (**Figure 2a**). Elution of *RR*-BF under the same conditions gave a single peak (**Figure 2b**) with retention time identical to that of peak I (**Figure 2a**). Therefore, *RR*-BF was eluted in front of the corresponding *1S-3S* enantiomer, and thermal conversion of enantiomers did not happen under the used conditions. Analysis of *cis*-PM also gave two well-separated, distinct peaks (**Figure 2c**), with retention times of 74.1 min (I) and 75.7 min (II). Because no enantiomer standard was available for *cis*-PM, it was only possible to infer the elution order of *cis*-PM enantiomers by referring to that of *cis*-BF enantiomers. Given that *cis*-PM closely resembles *cis*-BF structurally, and the chirality in both compounds derives from the 1C and 3C positions on the cyclopropyl ring (**Figure 1**), it is likely that the same elution order is obeyed by both *cis*-PM and *cis*-BF. Therefore, peak I in the *cis*-PM chromatogram was tentatively identified as *RR*-PM, and peak II as *SS*-PM (**Figure 2c**). During analysis of *cis*-PM, no peak was observed at the retention time of *trans*-PM, suggesting that conversion of *cis*-PM to *trans*-PM did not occur under the used conditions. **Figure 2** shows close to baseline separation of *cis*-BF enantiomers and complete baseline separation of *cis*-PM enantiomers under the conditions used in this study.

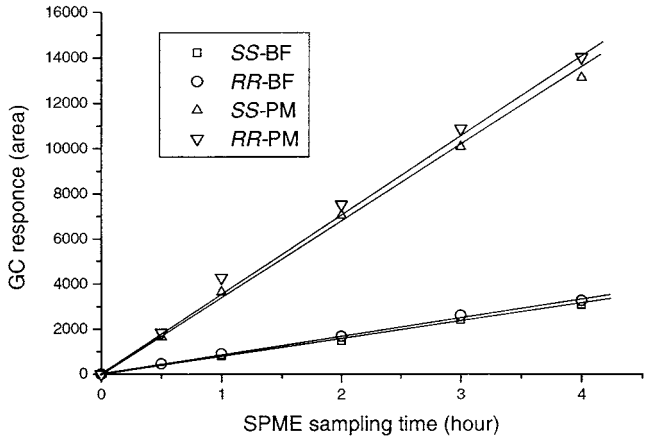

Figure 3. Dependence of GC response on SPME sampling time for analysis of *cis*-bifenthrin and *cis*-permethrin enantiomers (sampling temperature 20 ± 1 °C and enantiomer concentration 2.5 μg L^{-1}).

Optimization of Sampling Time. In developing optimized SPME sampling conditions, the most important step is determination of the time required to reach a thermodynamic equilibrium for the partition of the analyte between the aqueous phase and the SPME sorbent (*1*). The partition between the stationary and liquid phases may be described by

$$K = C_s/C_l \quad (1)$$

where K, C_s, and C_l are the partition coefficient, concentration in the SPME stationary phase, and concentration in the aqueous phase, respectively. Because GC analysis gives concentration in moles (n_s) of the target analyte per volume of the SPME stationary phase (V_s), eq 1 may be rewritten as

$$K = n_s/V_s\, C_l \quad (2)$$

With a given C_l, K will be a constant when equilibrium is reached between C_s and C_l. The value of K is related to the properties of the analyte as well as the SPME stationary phase, such as polarity and solubility, and environmental conditions such as temperature. As shown in **Figure 3**, equilibrium was not reached for either *cis*-BF or *cis*-PM enantiomers between the PDMS fiber and the aqueous phase during a 240-min equilibration period. This suggests that partition of pyrethroids on the PDMS fiber is a slow process, and increasingly greater sensitivity may be achieved if longer sampling time is used. On the other hand, because it is usually also desirable to maximize sample throughput, a key parameter in method optimization is the sample-to-sample GC run time, which in this study, was about 60 min for *cis*-BF and 85 min for *cis*-PM. Therefore, although improved sensitivity may be achieved with longer sampling time, 60 min was selected as the SPME sampling time in subsequent method optimization steps. The nonequilibrium sampling requires that sampling conditions, including SPME sampling time and sample constituents, be carefully controlled for achieving quantitative analysis.

Responses of enantiomers of the same compound were statistically similar ($\alpha = 0.05$) for both *cis*-BF and *cis*-PM (**Figure 3**). This result suggests that there was no selectivity between the 1*S*-3*S* and 1*R*-3*R* enantiomers during analyte enrichment on the PDMS fiber. The lack of selectivity may be attributed to the fact that enantiomers of a compound have similar physical and chemical properties and that PDMS has symmetric or achiral structure. Anderson et al. (*21*) evaluated adsorption of proteins (chiral molecules) on SPME adsorbents

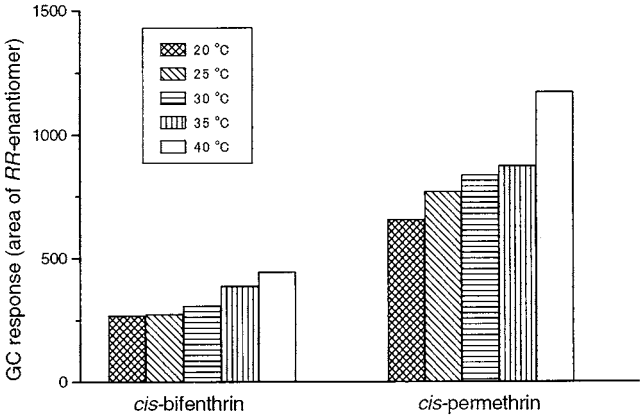

Figure 4. Effect of SPME sampling temperature on GC response for analysis of 1*R*-3*R*-bifenthrin and 1*R*-3*R*-permethrin (sampling time 30 min and enantiomer concentration 1.5 μg L^{-1}).

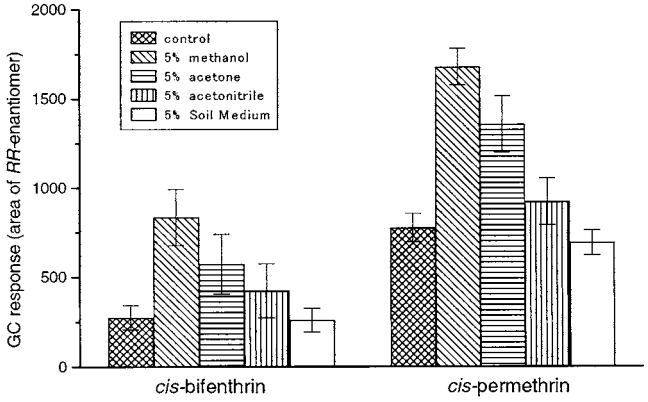

Figure 5. Effect of presence of organic solvents and soil components on GC response for analysis of 1*R*-3*R* bifenthrin and 1*R*-3*R*-permethrin (sampling temperature 20 ± 1 °C, sampling time 30 min, and concentration 1.0 μg L^{-1}).

and did not observe enantioselectivity. The nonselective behavior of SPME sampling for enantiomers is advantageous, because it preserves the original enantiomer composition in samples.

Effect of Sampling Temperature. As the solution temperature was increased from 20 to 40 °C, the GC response consistently increased (**Figure 4**). Compared to the signal output at 20 °C, the GC response at 40 °C was enhanced by 66% for *RR*-BF and by 78% for *RR*-PM. Similar increases were also observed for the 1*S*-3*S* enantiomers. In a previous study, temperature was found to shorten the time required for reaching equilibrium (*20*). Sensitivity of analysis of bifenthrin, permethrin, and deltamethrin consistently increased as temperature was increased from 30 to 90 °C (*20*). The increase in analyte enrichment on the SPME fiber by temperature may be attributed to enhanced diffusion of analyte molecules in the aqueous phase, resulting in accelerated partitioning into the SPME stationary phase. These observations suggest that temperature may be manipulated for improving analysis sensitivity when needed. However, high sampling temperature may cause decomposition of the target analyte or shifts in equilibrium when multiple phases are present (e.g., natural water samples containing particulates). The use of elevated sampling temperature must be further evaluated through method development.

Effect of Organic Solvents and Soil Components. Some aqueous samples, such as wastewater effluents and extracts of soil or other environmental samples, often contain impurities that include solvents and soil components. The effect of cosolvents and soil components on SPME-enantioselective GC analysis of *cis*-BF and *cis*-PM enantiomers was evaluated in this study. The presence of 5% of solvent in the aqueous phase consistently resulted in increased GC response, suggesting that enrichment of *cis*-BF or *cis*-PM enantiomers onto the PDMS fiber was enhanced by the solvents (**Figure 5**). Compared to the solvent-free control, the GC response of *RR*-BF in the solvent-amended samples increased by 204, 108, and 54% for methanol, acetone, and acetonitrile, respectively (**Figure 5**). The corresponding increases for *RR*-PM were 117, 75, and 19%. Similar increases were also observed for the 1*S*-3*S* enantiomers of *cis*-BF and *cis*-PM. The overall trend of solvent enhancement followed the order methanol > acetone > acetonitrile (**Figure 5**). The cause for the observed solvent effect was not clear from this study. It is likely that water-miscible solvents increased diffusion of the target analyte into the PDMS phase or reduced sorption of the analyte to the container surfaces. The GC response in the soil extract was slightly reduced when compared to the control (**Figure 5**). It is known that in SPME sampling, the freely dissolved concentration of the target analyte is selectively detected, and the presence of other phases (e.g., solid particulates or dissolved organic matter) may decrease the detectable concentration, especially for compounds that are strongly adsorbed to soil or sediment components (*9*). The limited effect of soil extract in this study may be due to the fact that only 5% of the soil extract was amended, and increased reduction in GC response may occur in concentrated soil extracts or for samples with higher organic matter content. The effects of solvents and soil components observed in this study suggest that the influence of the sample matrix needs to be considered in SPME-GC analysis. Suspended solids must be removed before SPME sampling, or calibration standards must be prepared in the same matrix as that of the sample.

Table 1. Method Detection Limit and Linear Ranges for Analysis of Enantiomers of Synthetic Pyrethroids *cis*-Bifenthrin and *cis*-Permethrin by Solid-Phase Microextraction and Enantioselective GC

	MDL (μg L^{-1})	linear range (μg L^{-1})	corr coeff (r^2)
cis-*S*,*R*-bifenthrin	0.05	0.05–20	0.97
cis-*S*,*R*-permethrin	0.10	0.10–20	0.98

Method Evaluation. The developed SPME- enantioselective GC method was further evaluated for method detection limits (MDLs) and linearity in analysis of enantiomers of *cis*-BF and *cis*-PM. When 60 min sampling time and 20 °C sampling temperature were used, the estimated MDL was 0.05 μg L^{-1} for *cis*-BF enantiomers and 0.10 μg L^{-1} for *cis*-PM enantiomers (**Table 1**). These MDL values were higher than those for SPME analysis of *cis*-BF and *cis*-PM on an achiral GC column, where the MDL was estimated to be 0.005 μg L^{-1} for *cis*-BF and 0.01 μg L^{-1} for permethrin isomers (*9*). The lower sensitivity for enantiomer analysis may be attributed to the fact that achiral analysis gives an unresolved peak for an enantiomer pair, while enantioselective analysis gives two separated peaks for an enantiomer pair. Enantioselective analysis of enantiomers of *cis*-BF or *cis*-PM required much longer run time than achiral analysis of the racemic mixtures, and the prolonged retention time may lead to a lower signal-to-noise ratio. As discussed previously, the method sensitivity may be further improved by using longer SPME sampling time, high temperature, or both. In the concentration range of 0.05−20 (*cis*-BF) or 0.10−20 μg L^{-1} (*cis*-PM), dependence of the GC response on analyte concentration was found to be linear for each enantiomer, with a

Table 2. Comparison of Liquid–Liquid Extraction (LLE) and Solid-phase Microextraction (SPME) for Analysis of *cis*-Bifenthrin and *cis*-Permethrin Enantiomers in Runoff Water Samples ($n = 3$)

		water samples					
		1	2	3	4	5	6
LLE (μg L-1)	*SS*-BF	0.94 ± 0.05	0.10 ± 0.04	0.09 ± 0.05	0.10 ± 0.04	0.08 ± 0.04	0.08 ± 0.04
	RR-BF	1.92 ± 0.06	0.22 ± 0.05	0.18 ± 0.04	0.21 ± 0.05	0.16 ± 0.04	0.14 ± 0.05
	SS-PM	0.09 ± 0.05	0.65 ± 0.04	ND	ND	ND	ND
	RR-PM	0.25 ± 0.04	1.11 ± 0.05	0.15 ± 0.04	0.11 ± 0.05	0.08 ± 0.04	0.12 ± 0.05
SPME (μg L-1)	*SS*-BF	0.35 ± 0.04	0.08 ± 0.04	0.05 ± 0.04	0.07 ± 0.05	ND	ND
	RR-BF	1.02 ± 0.05	0.12 ± 0.05	0.11 ± 0.05	0.15 ± 0.04	0.10 ± 0.04	0.07 ± 0.05
	SS-PM	ND	0.42 ± 0.04	ND	ND	ND	ND
	RR-PM	0.17 ± 0.05	0.72 ± 0.5	0.11 ± 0.04	ND	ND	ND

correlation coefficient $r^2 \geq 0.97$ and relative standard deviations 1.2−6.8% ($n = 5$).

The developed SPME method was compared to LLE for analysis of enantiomers of *cis*-BF and *cis*-PM in nursery runoff samples. The runoff samples contained small amounts of suspended solids, and the level of suspended solids varied from 5 to 50.5 mg L^{-1}, depending on the sampling location. Three replicate analyses were performed, using each method for the same sample, and the mean and standard error are listed in **Table 2**. Reproducibility was good for samples with relatively high concentrations but poor for samples with concentrations close to the MDL, and the overall trend was similar between the two extraction methods. The overall sensitivity was slightly lower for SPME than for LLE under the conditions specified for each method, and more no-detections were recorded for the SPME analysis. Concentrations detected in the first two samples were generally the highest for the resolved enantiomers (**Table 2**), which may be attributed to the close location of these samples to the inlet of the runoff channel. It was evident that the concentration of the 1*R*-3*R* enantiomer was consistently higher than that of the 1*S*-3*S* enantiomer for both *cis*-BF and *cis*-PM. This finding indicates that the 1*S*-3*S* enantiomer was preferentially degraded in the nursery environment, although the commercial formulations were racemic mixtures. Enantioselective degradation has been observed for other pesticides, including fungicide metalaxyl (*13*), insecticide α-hexachlorocyclohexane (α-HCH) (*14*), and herbicide dichlorprop (*10*). In soils, the fungicidally active *R*-enantiomer of metalaxyl was preferentially biodegraded over the *S*-enantiomer (*13*). Analysis of water and snow samples in and around an Arctic lake showed that the enantiomeric ratio of (+) α-HCH over (−) α-HCH deviated widely from the original value (1.0), suggesting active enantioselective degradation by microorganisms in the Arctic environment (*14*). Preferential transformation was also observed for the nonherbicidal enantiomer of dichlorprop in Brazilian pasture soils, while the herbicidal enantiomer was selectively degraded in forest soils (*10*). In this study, the concentration determined by SPME analysis was consistently smaller than that measured by LLE for the same sample (**Table 2**). The difference was apparently caused by adsorption of pesticides to the suspended solids in the runoff samples, as observed in a previous study using achiral analysis (*9*). Therefore, SPME-enantioselective GC analysis detected the freely dissolved fraction of *cis*-BF or *cis*-PM that may better reflect the bioavailable concentration. The MDLs and ranges of linearity observed in this study suggest that the developed method is suitable for analysis of synthetic pyrethroid enantiomers in environmental samples, such as runoff effluents, surface water samples, and soil or sediment samples.

Coupled SPME-chromatographic analysis has significant advantages when compared to some of the traditional solvent-based procedures. In particular, in SPME-GC (or HPLC) analysis, steps for sampling and analysis are streamlined, and no solvent is used. This study shows that SPME may be used together with enantioselective GC analysis for analysis of enantiomers in environmental samples. Enantiomers of *cis*-BF or *cis*-PM were equally enriched onto the PDMS phase, and the enrichment generally increased with increasing sampling time and temperature. On a β-cyclodextrin-based enantioselective column, enantiomers of *cis*-BF or *cis*-PM following SPME sampling were baseline separated, and evaluation of method sensitivity and reproducibility suggested that the developed SPME-enantioselective GC analysis may be used for detecting enantiomers of synthetic pyrethroids in water samples and soil extracts. In comparison with nonselective sample preparation techniques such as LLE, SPME was capable of selectively detecting the freely dissolved or bioavailable fraction of a contaminant in aqueous media. This feature allows the measured concentration to be potentially related to ecotoxicological endpoints such as aquatic toxicity or bioaccumulation potential. As many environmental contaminants are chiral compounds, the ability of SPME-enantioselective GC for determining enantiomers in environmental samples provides an additional application for the SPME sample preparation technique.

ACKNOWLEDGMENT

We thank FMC for providing analytical standards.

LITERATURE CITED

(1) Pawliszyn, J. *Solid-phase Microextraction: Theory and Practice*; Wiley-VCH: New York, 1997.
(2) Buchholz, K. D.; Pawliszyn, J. Determination of phenols by solid-phase microextraction and gas-chromatographic analysis. *Environ. Sci. Technol.* **1993**, *27*, 2844−2848.
(3) Zhang, Z.; Pawliszyn, J. Headspace solid-phase microextraction. *J. Anal. Chem.* **1993**, *62*, 1843−1852.
(4) Choudhury, T. K.; Gerhardt, K. O.; Mawhinney, T. P. Solid-phase microextraction of nitrogen and phosphorus-containing pesticides from water and gas chromatographic analysis. *Environ. Sci. Technol.* **1996**, *30*, 3259−3265.
(5) Goncalves, C.; Alpendurada, M. F. Comparison of three different poly(dimethylsiloxane) -divinylbenzene fibres for the analysis of pesticide multiresidues in water samples: structure and efficiency. *J. Chromatogr. A* **2002**, *963*, 19−26.
(6) Vaes, W. H. J.; Ramos, E. U.; Verhaar, H. J. M.; Seinen, W.; Hermens, J. L. M. Measurement of the free concentration using solid-phase microextraction: Binding to protein. *Anal. Chem.* **1996**, *68*, 4463−4467.
(7) Mayer, P.; Vaes, W. H. J.; Hermens, J. L. M. Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: High partition coefficients and fluorescence microscopy images. *Anal. Chem.* **2000**, *79*, 459−464.

(8) Mayer, P.; Vaes, W. H. J.; Wijnker, F.; Legierse, K. V. H. M.; Kraaij, R.; Tolls, J.; Hermens, J. L. M. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* **2000**, *34*, 5177−5183.

(9) Liu, W. P.; Gan, J.; Lee, S. J.; Kabashima, J. N. Phase distribution of synthetic pyrethroids in runoff and streamwater. *Environ. Toxic. Chem.* **2003** (in press).

(10) Lewis, D. L.; Garrison, A. W.; Wommack, K. E.; Whittemore, A.; Steudler, P.; Melillo, J. Influence of environmental changes on degradation of chiral pollutants in soils. *Nature* **1999**, *401*, 898−901.

(11) Kurihara, N.; Miyamoto, J. *Chirality in Agrochemicals*; John Wiley: Chichester, UK, 1998.

(12) Hegeman, W. J. M.; Laane, R. W. P. M. Enantiomeric enrichment of chiral pesticides in the environment. *Rev. Environ. Contam. Toxicol.* **2002**, *173*, 85−116.

(13) Falconer, R. L.; Bidleman, T. F.; Gregor, D. J.; Semkin, R.; Teixeira, C. Enantioselective breakdown of alpha-hexachlorocyclohexane in a small arctic lake and its watershed. *Environ. Sci. Technol.* **1995**, *29*, 1297−1302.

(14) Buser, H. R.; Müller, M. D. Occurrence and transformation reactions of chiral and achiral phenoxyalkanoic acid herbicides in lakes and rivers in Switzerland. *Environ. Sci. Technol.* **1998**, *32*, 626−633.

(15) Bidleman, T. F.; Falconer, R. L. Enantiomer ratios for apportioning two sources of chiral compounds. *Environ. Sci. Technol.* **1999**, *33*, 2299−2301.

(16) Wiberg, K.; Letcher, R. J.; Sandau, C. D.; Norstrom, R. J.; Tysklind, M.; Bidleman, T. F. The enantioselective bioaccumulation of chiral chlordane and alpha-HCH contaminants in the polar bear food chain. *Environ. Sci. Technol.* **2000**, *34*, 2668−2674.

(17) Leicht, W.; Fuchs, R.; Londershausen, M. Stability and biological activity of cyfluthrin isomers. *Pestic. Sci.* **1996**, *48*, 325−332.

(18) Boussahel, R.; Bouland, S.; Moussaoui, K. M.; Baud, M.; Montiel, A. Determination of chlorinated pesticides in water by SPME/GC. *Water Res.* **2002**, *36*, 1909−1911.

(19) Fernandez-Gutierrez, A.; Martinez-Vidal, J. J.; Arrebola-Liebanas, F. J.; Gonzalez-Casado, A.; Vilchez, J. L. Determination of endosulfan and some pyrethroids in waters by micro liquid−liquid extraction and GC-MS. *Fresenius J. Anal. Chem.* **1998**, *360*, 568−572.

(20) Barrionuevo, W. R.; Fancas, F. M. Solid-phase microextraction of pyrethroid pesticides from water at low and sub-ppt levels at different temperatures. *J. High Resol. Chromatogr*. **2000**, *23*, 485−488.

(21) Anderson, J. M.; Ziats, N. P.; Azeez, A.; Brunstedt, M. R.; Stack, S.; Bounfield, T. L. protein adsorption and macrophage activation on poly(dimethylsiloxane) and silicone-rubber. *J. Biomaterials Sci.-Poly. Ed.* **1995**, *7*, 159−169.

Received for review October 31, 2003. Revised manuscript received December 16, 2003. Accepted December 17, 2003. This study was supported by California Department of Food and Agriculture, agreement No. 02-0741.

JF035276F