

# Development of a Solid-Phase Microextraction-Based Method for Sampling of Persistent Chlorinated Hydrocarbons in an Urbanized Coastal Environment

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Solid-phase microextraction (SPME) has been used as an in situ sampling technique for a wide range of volatile organic chemicals, but SPME field sampling of nonvolatile organic pollutants has not been reported. This paper describes the development of an SPME-based sampling method employing a poly(dimethylsiloxane) (PDMS)-coated (100- $\mu$ m thickness) fiber as the sorbent phase. The laboratory-calibrated PDMS-coated fibers were used to construct SPME samplers, and field tests were conducted at three coastal locations off southern California to determine the equilibrium sampling time and compare the efficacy of the SPME samplers with that of an Infiltrax 100 water pumping system (Axys Environmental Systems Ltd., Sidney, British Columbia, Canada). *p,p'*-DDE and *o,p'*-DDE were the components consistently detected in the SPME samples among 42 polychlorinated biphenyl congeners and 17 chlorinated pesticides targeted. SPME samplers deployed at two locations with moderate and high levels of contamination for 18 and 30 d, respectively, attained statistically identical concentrations of *p,p'*-DDE and *o,p'*-DDE. In addition, SPME samplers deployed for 23 and 43 d, respectively, at a location of low contamination also contained statistically identical concentrations of *p,p'*-DDE. These results indicate that equilibrium could be reached within 18 to 23 d. The concentrations of *p,p'*-DDE, *o,p'*-DDE, or *p,p'*-DDD obtained with the SPME samplers and the Infiltrax 100 system were virtually identical. In particular, two water column concentration profiles of *p,p'*-DDE and *o,p'*-DDE acquired by the SPME samplers at a highly contaminated site on the Palos Verdes Shelf overlapped with the profiles obtained by the Infiltrax 100 system in 1997. The field tests not only reveal the advantages of the SPME samplers compared to the Infiltrax 100 system and other integrative passive devices but also indicate the need to improve the sensitivity of the SPME-based sampling technique.

## Introduction

Global distribution of persistent organic pollutants (POPs) has been a subject of many research and monitoring activities

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(1–7). A previous study suggests that regional and global dynamics of POPs are mainly controlled by oceanic biogeochemical processes (8). Such a notion emphasizes the importance of quantifying POPs in oceanic environments. Moreover, dissolved phase POPs are likely available for bioaccumulation by aquatic species, which further dissipates POPs into a wide range of environmental compartments. Of particular ecological significance among this class of chemicals are persistent chlorinated hydrocarbons such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (e.g., DDTs). Detection of these constituents in open aquatic environments, however, is a difficult task. For example, concentrations of *p,p'*-DDE, an abundant component among the commonly found POPs in the environment, ranged from 0.0001 to 0.008 ng/L in surface water of open seas and oceans (9).

To achieve sufficient sensitivity, several large-volume sampling strategies, such as on-board filtration/resin extraction (10, 11), on-board filtration/liquid–liquid extraction (12, 13), on-board centrifuging (14), and in situ water pumping (15–18), have been employed in field studies. These sampling methods, however, are either labor-intensive or costly to implement and are not feasible as a simultaneous sampling technique for most large-scale sampling programs. In recent years, an integrative passive sampling technique based on semipermeable membrane devices (SPMD) has been developed (19). SPMDs appear to have overcome many of the drawbacks of the large-volume sampling approaches, but calibration, sample processing, and data interpretation are still involved (19–23).

An alternative sampling strategy could be developed based on SPME. Commonly used SPME analytical methods employ a fused silica fiber coated with a specific polymeric phase. Extraction proceeds when the polymer-coated fiber is directly introduced to the sample matrix or the headspace above it, and quantitation is performed based on the distribution of the analyte between the polymeric phase and the sample matrix or headspace. SPME-based methods are simple to use and cost-effective, and, more importantly, the quantitative aspects of SPME are straightforward if equilibrium is attained. As a result, SPME has found broad application (24, 25) since it was introduced as a quantitative analytical tool in 1990 (26). One particularly beneficial application is field sampling, as SPME samplers are easy to construct and convenient to operate during field cruises. However, efforts to develop SPME-based analytical and sampling protocols have so far been focused on volatile organic chemicals (VOCs). This is readily justified, because depletion of VOCs in a sample by the sorbent phase is often negligible, which results in a simple procedure for quantitation (27). Conversely, SPME field sampling of nonvolatile organic compounds (e.g., POPs) in aquatic environments has not been reported.

This study was initiated to develop an SPME sampling method with the capacity to detect subparts per trillion levels of persistent chlorinated hydrocarbons in open oceans, and the objectives were as follows: (1) to determine the equilibrium sampling time; (2) to evaluate the detection limits; and (3) to assess the sampling efficacy. The first objective was fulfilled through examination of the sampling efficiency of SPME samplers deployed for different time periods at the same location. The second and third objectives were accomplished by comparing the performance of the SPME samplers and an in situ water pumping system (16–18). The sampling locations (Figure 1) representing different levels of DDT contamination within the Southern California Bight were surveyed previously with the in situ water pumping

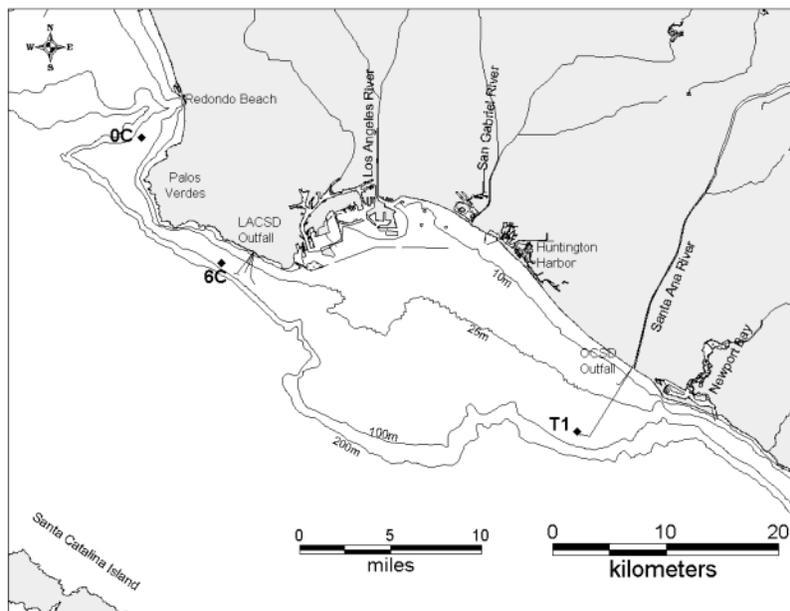


FIGURE 1. Map of the sampling locations off the coast of southern California. Stations 6C and T1 are adjacent to the outfalls of the Los Angeles County Sanitation District (LACSD) and the Orange County Sanitation District (OCSD), respectively.

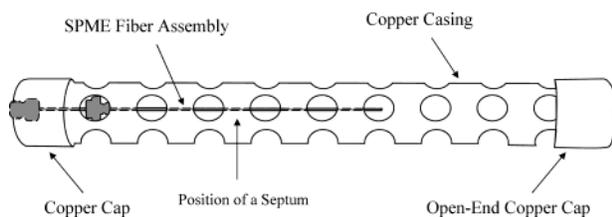


FIGURE 2. Schematic of the SPME-based sampling device.

system (16, 17). Results from these previous studies were therefore included for comparison.

## Methods

**Construction of SPME Samplers.** A typical SPME sampler consists of a 100- $\mu\text{m}$  PDMS-coated fiber assembly (part no. 57341-U; Supelco, Bellefonte, PA) and a 15  $\times$  1.5 cm copper casing with 8-mm holes (Figure 2). The holes allow water circulation around the PDMS-coated fiber. The copper casing protects the PDMS-coated fiber from physical collision with large objects and slows bacterial growth. The fiber assembly is attached to a copper end-cap sealing one end of the casing. The other end of the casing is covered with a 1-cm hollowed copper end-cap. The fiber assembly is suspended within the copper casing and supported with a Teflon-lined septum around the stainless steel sleeve housing the fiber. Prior to field deployment, all copper casings were sonicated in a methylene chloride:methanol (1:1) mixture for 20 min and in hexane for another 20 min, dried at ambient temperatures, and wrapped in aluminum foil until assembled with SPME fibers. The assembled SPME samplers were wrapped in aluminum foil and stored at  $-20^\circ\text{C}$ .

**Field Deployment.** Deployment of SPME samplers was conducted from May to November of 2003 at three coastal locations, stations 6C and 0C off Palos Verdes and T1 near the outfall of the Orange County Sanitation District (OCSD) (Figure 1). Immediately before deployment, each PDMS-coated fiber was extruded from its protective sleeve and immersed into hexane for final cleaning. Each sampling device was attached to a 6.4-mm twisted polypropylene rope with stainless steel hose clamps. The whole mooring unit was anchored by chain links and suspended in the water column with a subsurface float (Figure 3). Upon completion

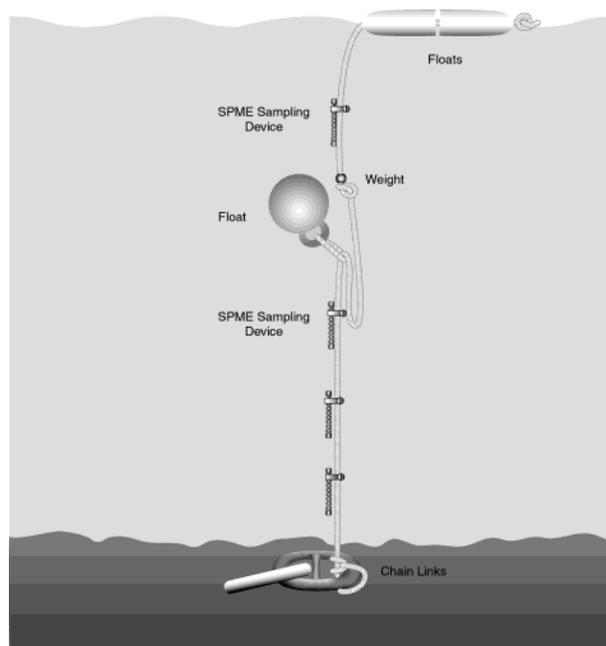


FIGURE 3. Schematic showing the field deployment of SPME samplers at various depths in the water column.

of deployment, each SPME sampler was carefully removed from the mooring, and the fiber assembly was detached from the copper casing. The PDMS-coated fiber tip was rinsed briefly with deionized water to remove any visible attached particles and retracted into the protective sleeve. The fiber assembly was placed into an aluminum foil lined Petri dish and cooled with dry ice during transportation to the laboratory. All fiber assemblies were stored at  $-20^\circ\text{C}$  until analysis.

A parallel sampling employing the Infiltrax 100 system was conducted at stations 6C and T1 (Figure 1). The operating procedures for this in situ sampling method as well as its main features as a large-volume sampler were described previously (16–18). One sample each was collected from 6C and T1 with the volumes of water processed being 999 and 1737 L, respectively.

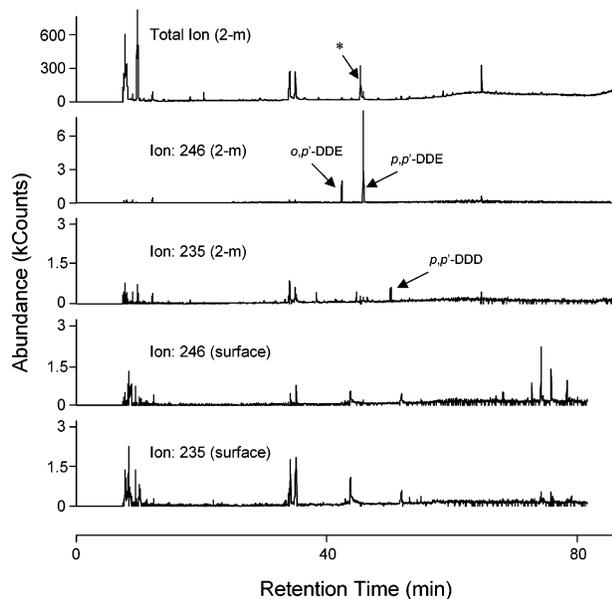


FIGURE 4. Chromatograms of two SPME samples collected from station 6C (Figure 1) at 2 m from the sediment–water interface and below the sea surface, respectively. \*: Comparison to the NIST reference library indicated that this peak was derived from 4,4'-(1-methylethylidene)bisphenol.

**Sample Analysis.** Analytes sorbed on the PDMS-coated fibers were thermally desorbed into a Varian 2000 GC/ion trap-MS system (Varian Inc., Walnut Creek, CA) for quantitation. Detailed experimental parameters were given elsewhere (28), and only a brief description is presented here. A PDMS-coated fiber was inserted into the GC injection port (programmed from 100 to 280 °C at ~100 °C/min and held for 40 min) and subject to desorption for 2.5 min. A 60 m × 0.25 mm-i.d. (0.25 μm film thickness) DB-5MS column used for chromatographic separation was temperature-programmed from 80 °C (held for 1 min) to 176 °C at 8 °C/min, to 230 °C at 1.5 °C/min, and to 290 °C at 5 °C/min (held for 21 min). Mass spectra were acquired from 100 to 504 *m/z* with a scan rate of 0.7 scans per second and an emission current of 15 μamps. Figure 4 depicts chromatograms of two SPME samples collected at 2-m depth from the sediment–water interface and sea surface, respectively, of station 6C.

The SPME-based sampling method only measures organic chemicals in the dissolved phase, whereas the Infiltrax 100 system obtains both the particulate and dissolved phase (operationally defined as filtrates passing through a 0.7 μm glass fiber filter) materials. In this study, only the dissolved phase concentrations from both sampling methods were compared. Dissolved organics retained by the XAD-II resin-packed Teflon columns were eluted and analyzed using the procedure described previously (16). The instrumental analysis was conducted using the same GC/MS procedure as described above, except that injection of solvent-prepared samples was automated with a Varian 8100 autosampler.

**QA/QC Performance.** Each SPME fiber was rinsed with hexane and baked at 280 °C under helium stream for 1 h prior to use. Analysis of selected freshly baked SPME fibers indicated no carry-over of any target analyte. Two SPME samplers were deployed at 2 m from the sea surface at station 6C and treated as blank samples, and no detectable target analytes were detected. Only residues leaching from the PDMS coating phase were observed (one sample chromatogram is displayed in Figure 4). During each of the two field trips to deploy the Infiltrax 100 system, a Teflon column filled with XAD-II resins was also carried through and processed as field blank. The field blanks contained no

detectable target analytes. One filled Teflon column was spiked with the target analytes and processed as a sample. The average recovery of all the target analytes was 77.7 ± 10.1%. Finally, surrogate standards of tetrachloro-*m*-xylene, PCB 65, and PCB 209 were spiked into all Infiltrax-related samples (two field samples, two blanks, and one blank spike) prior to extraction. The recoveries were 61.8 ± 5.4, 78.3 ± 5.4, and 72.9 ± 8.8% for tetrachloro-*m*-xylene, PCB 65, and PCB 209, respectively. Recovery correction was not made for the analyte concentrations.

**Data Analysis.** Quantitation of an analyte in the SPME samples was based on the relationship between the amount of the analyte sorbed in the PDMS phase ( $N_f$ ) and the concentration ( $C_w^0$ ) in the sample matrix (seawater in the present study) (29)

$$N_f = \frac{K_f V_f (V_w + K_H V_h)}{K_f V_f + V_w + K_H V_h} C_w^0 \quad (1)$$

where  $K_f$  is the distribution coefficient for the analyte between the PDMS phase and seawater,  $V_f$ ,  $V_w$ , and  $V_h$  are the volumes of the PDMS phase, seawater, and headspace (atmosphere in this case), respectively, and  $K_H$  is the dimensionless Henry's Law constant. In open oceans,  $V_w \gg K_f V_f$  and  $K_H V_h$ . Therefore, eq 1 can be simplified to

$$N_f = K_f V_f C_w^0 \quad (2)$$

Apparently, the concentrations of the target analytes can be directly calculated from predetermined  $K_f V_f$  values and the measured amounts of the analytes in the PDMS phase. In this study, all the SPME samplers were processed with the same analytical instrument designated as GC-MS-1 in a separate publication (28) to ensure consistency throughout the study. Therefore the  $K_f V_f$  values determined with this instrument were used for quantitation. Specifically, the  $K_f V_f$  values for *p,p'*-DDD, *o,p'*-DDE, and *p,p'*-DDE, the only components detected in the SPME samples, were 9.76(±0.67) × 10<sup>4</sup>, 5.82(±1.81) × 10<sup>5</sup>, and 3.41(±0.54) × 10<sup>5</sup> μL, respectively (28). The reporting limits for the SPME samples were estimated from eq 2, but  $N_f$  was set to the lowest calibration amount (0.025 ng) in the solvent-prepared standards, and  $C_w^0$  in this specific situation was designated as the reporting limit. As a result, reporting limits for the SPME sampling method varied with individual target analytes (Table 1). Reporting limits for the Infiltrax samples were 0.050 (6C) and 0.029 (T1) ng/L, calculated from the sample volumes (999 and 1737 L) and the second lowest calibration amount (0.05 ng). The selection of the second lowest amount was based on the fact that the Infiltrax samples contained slightly higher background interferences than the SPME samples.

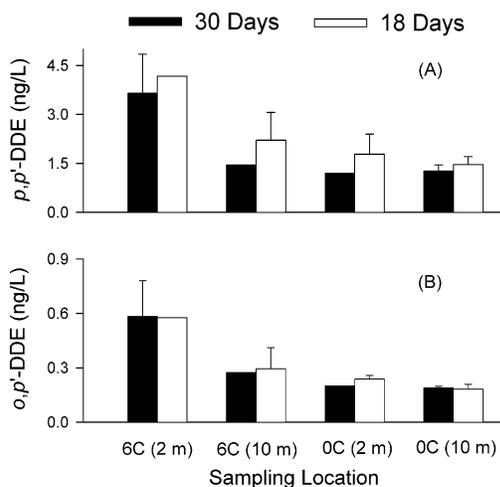
## Results

**Equilibrium Deployment Time.** Deployment times were compared at all three sampling locations (Figure 1) at the 2- and 10-m depths. The range of deployment times used for comparison was estimated from kinetic experiments reported elsewhere (28) prior to field cruises. An exposure time of 12 d and an agitation velocity of ~4 cm/s were sufficient for all the target analytes to achieve equilibrium between the particulate and dissolved phases. The agitation velocity, determined from the radius of the stirring bar, the revolutions per second of the stirring bar, and the distance between the center of the experimental container and the PDMS-coated fiber (27), was in the approximate range of the median near-bottom current velocities (~3.7–12.3 cm/s) in southern California (30). Therefore, deployment times of slightly longer than 12 d were selected for field sampling.

**TABLE 1. Comparison of Dissolved Phase Concentrations (ng/L) of PCB Congeners and Chlorinated Pesticides Obtained with an Infiltrax 100 Water Pumping System and SPME Samplers at the 2-m Water Depth of Stations 6C and T1 (Figure 1)**

analyte	6C (2 m)				T1 (2 m)			
	pumping (999 L)	SPME (18 d)	SPME#1 (30 d)	SPME#2 (30 d)	pumping (1737 L)	SPME#1 (43 d)	SPME#2 (43 d)	reporting limit for SPME (ng/L)
PCB 28	0.075	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.24
PCB 37	0.22	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.20
PCB 44	0.050	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.13
PCB 52	0.052	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.13
PCB 66	0.051	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.11
PCB 70	0.054	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.12
PCB 200	0.054	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.15
<i>o,p'</i> -DDD	0.090	<i>a</i>	<i>a</i>	<i>a</i>	<0.029	<i>a</i>	<i>a</i>	0.18
<i>p,p'</i> -DDD	0.40	0.39	0.56	0.72	<0.029	<i>a</i>	<i>a</i>	0.26
<i>o,p'</i> -DDE	0.80	0.58	0.44	0.72	<0.029	<i>a</i>	<i>a</i>	0.043
<i>p,p'</i> -DDE	3.2	4.2	2.8	4.5	0.11	0.060 <sup>b</sup>	0.099	0.073

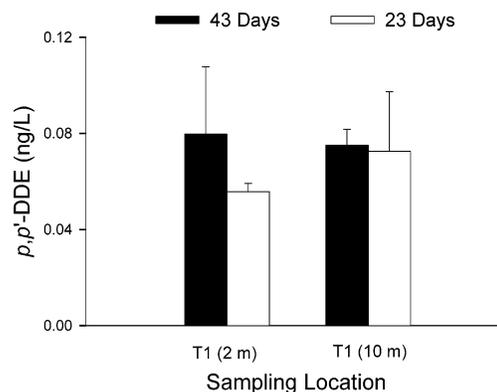
<sup>a</sup> Not detected at the respective reporting limits. Additional target analytes not detected in all samples include (the numbers in the parentheses are reporting limits (ng/L) for the SPME sampling method; the reporting limits for the 6C and T1 pumping samples were 0.050 and 0.029 ng/L, respectively) the following: PCB 18 (0.32); 49 (0.12); 74 (0.12); 77 (0.064); 81 (0.098); 87 (0.11); 99 (0.11); 101 (0.10); 105 (0.074); 110 (0.11); 114 (0.084); 118 (0.087); 119 (0.11); 123 (0.089); 126 (0.076); 128 (0.12); 138 (0.13); 149 (0.11); 151 (0.092); 153/168 (0.14); 156 (0.49); 157 (0.16); 158 (0.12); 167 (0.17); 169 (0.17); 170 (0.37); 177 (0.28); 180 (0.34); 183 (0.18); 187 (0.28); 189 (0.39); 194 (0.77); 201 (0.67); and 206 (1.3) and aldrin (0.047);  $\alpha$ -chlordane (0.12);  $\gamma$ -chlordane (0.11); chlordene (0.068); chlorpyrifos (0.91); diazinon (5.2); dieldrin (0.43); endrin (0.97); *cis*-nonachlor (0.16); *trans*-nonachlor (0.087); oxychlordane (0.086); *o,p'*-DDT (0.080); and *p,p'*-DDT (0.094). <sup>b</sup> The concentration was slightly lower than the reporting limit (0.073 ng/L), but comparison with the analysis of the standard solution and reference library (NIST) confirmed the presence of the compound.



**FIGURE 5. Water column concentrations of (A) *p,p'*-DDE and (B) *o,p'*-DDE obtained with SPME samplers for two timepoints at the 2- and 10-m depths of stations 6C and 0C (Figure 1). Sampling was conducted in May–June 2003.**

The results indicate that deployment times of 18 and 30 d yielded statistically indistinguishable concentrations of *p,p'*-DDE (Figure 5A) and *o,p'*-DDE (Figure 5B) at the 2- and 10-m depths of stations 6C and station 0C. These two locations are representatives of high and moderate DDT contamination, respectively, in the Southern California Bight. It is interesting to note that while the concentrations of both *p,p'*-DDE and *o,p'*-DDE were substantially different between the 2- and 10-m depths of station 6C, there was no statistical difference between the depths at station 0C. At station T1, a relatively clean area, only *p,p'*-DDE was detectable, and its concentrations were also similar at both the 2- and 10-m depths for deployment times of 23 and 43 d (Figure 6). These comparisons suggest that equilibrium sampling by the SPME samplers in the coastal ocean off southern California could be achieved within 18–23 d or less.

**Detection Capability of the SPME-Based Sampling Method.** Concentration distributions of individual PCB congeners and chlorinated pesticide in two Infiltrax samples and five SPME samples collected from the 2-m depth of stations 6C and T1 (Figure 1) are reflective of the detection limits for these two sampling methods (Table 1). While no



**FIGURE 6. Water column concentrations of *p,p'*-DDE obtained with SPME samplers deployed for two timepoints at 2- and 10-m depths of station T1 (Figure 1). Sampling was conducted in June–July 2003.**

PCB congeners were detected in the SPME samples, the in situ pump sample collected from station 6C contained several detectable PCB congeners (PCB 28, 37, 44, 52, 66, 70, and 200). The concentrations of these PCB congeners were near or slightly above the reporting limit of 0.050 ng/L, but generally below their respective SPME reporting limits. The exception was PCB 37 whose concentration was 0.22 ng/L, just above the reporting limit of 0.20 ng/L for the SPME samples.

Among the chlorinated pesticides, all non-DDT compounds were not detectable in both the SPME and in situ pump samples, and the distributions of DDT components were fairly similar in these two types of samples (Table 1). At station 6C, the in situ pump sample contained detectable *o,p'*- and *p,p'*-isomers of DDE and DDD. The SPME samples contained detectable *o,p'*- and *p,p'*-DDE and *p,p'*-DDD but not *o,p'*-DDD. This is again due to higher reporting limit (0.18 ng/L) for *o,p'*-DDD with SPME samples than its concentration (0.090 ng/L) in the in situ pump sample. At station T1, both the SPME and in situ sampling methods detected *p,p'*-DDE only. One of the SPME samples obtained *p,p'*-DDE at the concentration (0.060 ng/L) slightly below its reporting limit (0.073 ng/L). This concentration was reported, because the presence of *p,p'*-DDE in the SPME sample was confirmed with the NIST reference library, in addition to a

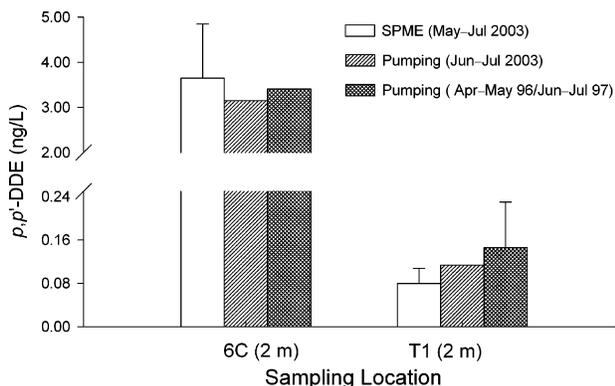


FIGURE 7. Water column concentrations of *p,p'*-DDE obtained with SPME samplers and an Infiltrax 100 water pumping system at the 2-m depth of stations 6C and T1 (Figure 1).

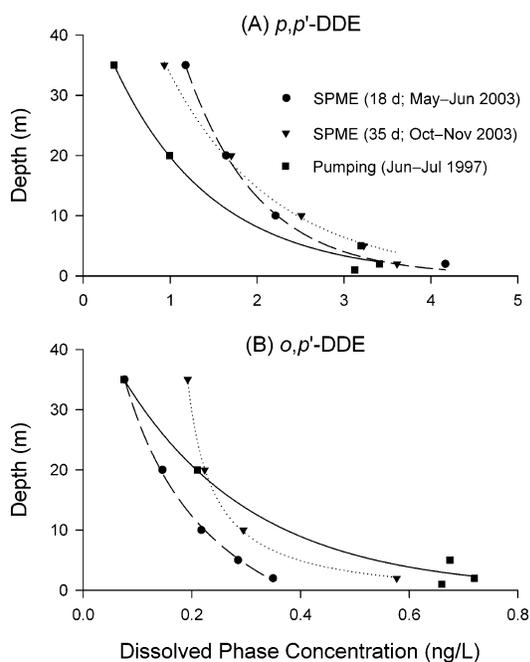


FIGURE 8. Water column vertical profiles of (A) *p,p'*-DDE and (B) *o,p'*-DDE at station 6C (Figure 1) obtained with SPME samplers and an Infiltrax 100 water pumping system. The sediment–water interface was defined as depth 0.

good agreement between the retention times for the SPME sample and the solvent-prepared standard analyzed prior to the sample analysis.

**Efficacy of the SPME-Based Sampling Method.** The efficacy of SPME samplers was assessed against that of the Infiltrax 100 system deployed at the 2-m depth of stations 6C and T1 (Figure 7). Results from two previous samplings (16, 17) using the Infiltrax 100 system were also included for comparison. The concentrations of dissolved phase *p,p'*-DDE were ~3.5 and 0.1 ng/L in samples collected from stations 6C and T1, respectively. It is apparent that both sampling methods obtained similar concentrations of *p,p'*-DDE at two locations of vastly different contamination levels.

Additional comparison between the SPME samplers and Infiltrax 100 system was conducted at multiple water column depths of station 6C. Concentration profiles of *p,p'*-DDE and *o,p'*-DDE were obtained with the SPME samplers in May–June and October–November 2003, respectively. These profiles all exponentially decreased with increasing distance from the sediment–water interface, similar to those obtained with the Infiltrax 100 system in June–July 1997 (Figure 8). A common feature for all these concentration profiles is that

the concentrations of *p,p'*-DDE or *o,p'*-DDE obtained with both the SPME and Infiltrax sampling methods were comparable near the sediment–water interface.

## Discussion

This study, for the first time to our best knowledge, successfully employed a SPME-based method for sampling persistent chlorinated hydrocarbons from an oceanic environment. The field tests provided valuable information for assessing the operational and quantitative facets of the SPME-based sampling strategy. One aspect is the quantitative variability as reflected in the results from replicate sample analyses. The average relative standard deviation was 23% from 14 replicate measurements (nine replicates for *p,p'*-DDE and five for *o,p'*-DDE; Figures 5–7). This variability was mostly accounted for by the uncertainties associated with the determination of  $K_f V_f$  values, as the average relative error of the  $K_f V_f$  values for *p,p'*-DDE and *o,p'*-DDE was 23%. In addition, the dynamic nature of the sampling environment may also have contributed to the sampling variability. It is interesting to note that the average relative standard deviation for the Infiltrax sampling method was 24% from four replicate measurements of total DDTs in both the dissolved and particulate phases (16).

Another aspect is the efficacy of the SPME sampling method, which was consistent with that of a large-volume sampling technique employing an Infiltrax 100 system (Figures 7 and 8). Comparing to the Infiltrax 100 system, the use of SPME samplers is clearly advantageous in two areas. The first is the cost-effectiveness associated with the construction and field operation of SPME samplers. Each SPME sampler costs less than \$100 to construct, whereas the price tag for an Infiltrax 100 system is approximately \$20 000. Operating expenses for the SPME sampling method were also much lower than those for the water pumping method. The second area is the substantial reduction of workload in handling and processing SPME samples. SPME samples can be processed directly via thermal desorption followed by analysis with an analytical instrument (e.g., GC/MS), whereas water pumping samples, like other conventional environmental samples, have to undergo a lengthy process of extraction, cleanup/fractionation, and condensation before becoming suitable for instrumental analysis.

It is also interesting to compare the SPME sampling method with SPMD-based sampling approaches. The SPMD technology was first introduced by Huckins and co-workers (31) and has since undergone extensive development (19, 21). Triolein has been widely used as a sorbent phase mainly because (1) it is an important component of fish lipids; (2) triolein–water partition coefficients ( $K_{tw}$ ) are highly correlated with readily available octanol–water partition coefficients ( $K_{ow}$ ); (3) high molecular weight of triolein greatly reduces membrane permeability; and (4) high-purity triolein is commercially available (19). SPMDs using PDMS and  $C_{18}$  Empore disk as sorbent phases have also been developed (32–34). In general, the sensitivity of SPMDs is superior over that of SPME samplers, simply because of the much larger sorbent phase (generally ~1 mL) often employed in SPMDs than that (~0.6  $\mu$ L for a 100- $\mu$ m coating thickness, the largest commercially available) used with SPME samplers. Calibration of SPMDs also appears less painful than SPME samplers as  $K_{tw}$  values for a large number of compounds can be determined by their correlation with  $K_{ows}$  (35), although determination of  $K_{ow}$  values has remained problematic for hydrophobic organic compounds (36). On the other hand, the membrane design with SPMDs intrinsically results in slower sorption of analytes into the sorbent phase. For example, equilibrium accumulation was not achieved even after 100 d of deployment for compounds with  $\log K_{ow} > 6$  (23). By contrast, deployment time of ~18 d with SPME

samplers appeared sufficient for equilibrium sampling of *p,p'*- and *o,p'*-DDE (Figures 5 and 6). As a result of the slow kinetics with SPMDs, quantitation is usually performed under nonequilibrium situations. This requires accurate determination of sampling rates for specific chemicals on specific SPMDs. Furthermore, SPMD samples have to undergo extensive postdeployment treatment (e.g., solvent dialysis, cleanup, fractionation, and concentration) prior to instrumental analysis. By contrast, the SPME samples acquired in the present study were processed directly without any pretreatment. We observed no interferences with the GC/MS measurements of *p,p'*- and *o,p'*-DDE and *p,p'*-DDD in any SPME samples (e.g., Figure 4).

The field deployments conducted in this study call for improvements to the SPME-based sampling method in two areas. The first is the inadequate capability of SPME samplers in detecting most of the target analytes (Table 1). As shown in eq 2, the capacity (volume) of the PDMS phase directly dictates the detection limit achievable with SPME samplers for a specific analyte. Apparently large sorbent phase volumes are required to increase sorption capacity (assuming equilibrium extraction is achieved). However, a large sorbent phase may result in slow sorption kinetics, subjecting SPME samplers to extended deployment durations. Without substantial enhancement of the detection limits, the SPME sampling method is viable only in moderately contaminated oceanic regions with the levels of persistent chlorinated hydrocarbons equal to or greater than ~0.1 ng/L. Future research should be directed toward developing new coating procedures to produce SPME fibers of high coating volume with large surface areas. The second area for improvement is the vulnerability of SPME samplers to rough conditions in oceanic environments. The main problem often encountered in our study was rupture in the joints between the polymer-coated fiber and the stainless steel supporting needle and between the supporting needle and the hub, occurring often after an extended field deployment. Nevertheless, the low cost of constructing and operating SPME samplers makes it feasible to simultaneously sample at multiple depths of the water column on a large spatial scale.

The limited field data acquired in this study suggest that DDTs, mainly *p,p'*-DDE and *o,p'*-DDE, are noticeably widespread in the coastal waters off Palos Verdes and Orange County. Furthermore, the exponentially decreasing concentrations of *p,p'*-DDE and *o,p'*-DDE with increasing distance from the sediment–water interface at station 6C (Figure 8) indicate that sediments remain the main source of DDT compounds to the water column, a view originally derived from the 1997 sampling (16) and subsequently subject to heated debates (37, 38). Sediments on the Palos Verdes Shelf are known to contain high levels of DDTs (39, 40). The mass inventory of DDTs, however, is believed to have decreased gradually over the last 30 years. For example, the DDT mass reduction was estimated to be in the order of 10–20 t/yr from 1972 to 1992 (41, 42). This reduction has been hypothesized to occur via two routes. The first route is in situ biodegradation (43, 44) that transforms DDE, the main component of the DDT mixture in sediments, to DDMU. However, this hypothesis has been shown to account for at most less than half of the decrease of the DDE mass (45). The second route of the mass reduction is via physical processes, such as resuspension, dispersion, and advection, etc. (16, 46). With the cost-effective SPME samplers, it is possible to measure the large-scale spatial distribution of DDTs in waters of the Southern California Bight, from which the fate of these persistent and potentially toxic compounds can be inferred.

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