Development of a solid-phase microextraction-based method for sampling of persistent chlorinated hydrocarbons in oceanic environments

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ABSTRACT - 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 non-volatile organic pollutants has not been reported. This paper describes the development of a SPME-based sampling method employing a polydimethylsiloxane (PDMS)-coated (100-mm 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 Infiltrex 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, obtained 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 Infiltrex 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 Infiltrex 100 system in 1997. The field tests revealed the advantages of the SPME samplers compared to the Infiltrex 100 system and other integrative passive devices, but also indicated the need to improve the detection capacity of the SPME-based sampling technique.

INTRODUCTION

Global distribution of persistent organic pollutants (POPs) has been a subject of many research and monitoring activities (Wania and Mackay 1995, Wania and Mackay 1996, 1999, Koziol and Pudykiewicz 2001, Ballschmitter *et al.* 2002, Fernández and Grimalt 2003, Lammel and Semeena 2003), apparently attributed to the unique physical, chemical, and ecotoxicological properties of POPs (Jones and de Voogt 1999). A previous study suggests that regional and global dynamics of POPs is mainly controlled by oceanic biogeochemical processes (Dachs *et al.* 2002). Such a notion emphasizes the importance of quantifying POPs in oceanic environments. Moreover, freely bound 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 (Iwata *et al.* 1993).

Traditional sampling methods, such as those employing regular size containers (e.g., Niskin bot-

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tle), are inadequate in achieving the detection capability required to quantify PCBs and DDTs at ultralow levels. Several large-volume sampling strategies, such as on-board filtration/resin extraction (Prats *et al.* 1992, Kannan *et al.* 1998), on-board filtration/liquid-liquid extraction (de Lappe *et al.* 1983, Pearson *et al.* 1996), on-board centrifuging (Domagalski and Kuivila 1993), and in-situ water pumping (Green *et al.* 1986, Zeng *et al.* 1999, Zeng *et al.* 2002, Zeng and Tran 2002) have been employed in field studies. These sampling methods, however, are either labor-intensive to operate or costly to implement, and are not feasible for large-scale sampling programs. In recent years, an integrative passive sampling technique based on semipermeable membrane devices (SPMD) has been developed (Lu *et al.* 2002). SPMDs appear to have overcome many of the drawbacks with the large-volume sampling approaches, but calibration, sample processing, and data interpretation are still considerably involved (Gale 1998, Petty *et al.* 2000, Lu *et al.* 2002, Luellen and Shea 2002, Louch *et al.* 2003).

An alternative sampling strategy could be developed based on the principles of SPME. Commonly used SPME-based analytical methods employ a glass fiber coated with a specific polymeric phase. Extraction proceeds with the polymer-coated fiber directly dipping into 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; more importantly, the quantitative aspects of SPME are straightforward if equilibrium state is attained. As a result, SPME has found broad applications (Pawliszyn 1999, Heringa and Hermens 2003) since it was introduced as a quantitative analytical tool in 1990 (Arthur and Pawliszyn 1990). One particularly beneficial application is field sampling, as SPME samplers are easy to construct and convenient to operate during field cruises. However, the 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 (Pawliszyn 1997). Conversely, SPME field sampling of non-volatile organic compounds (e.g., POPs) in aquatic environments has not been reported.

This study was commenced to develop an SPME-based sampling method with the capacity to detect sub-parts per trillion levels of persistent chlorinated hydrocarbons in open oceans. Field studies were conducted at three coastal sites (Figure 1) representing different levels of DDT contamination within the Southern California Bight to test the utility of the SPME samplers with the following objectives: (1) to determine the equilibrium sampling time; (2) to evaluate the detection capability; and (3) to assess the sampling efficacy. The first objective was fulfilled with an examination of the sampling efficiency of SPME samplers deployed for different time durations at the same location. The second and third objectives were accomplished by comparing the performance of the SPME samplers and the Infiltrex 100 system. The sampling locations selected in this study were surveyed previously with the Infiltrex 100 system (Zeng *et al.* 1999, Zeng and Tran 2002). Results from these previous studies were therefore included for comparison.

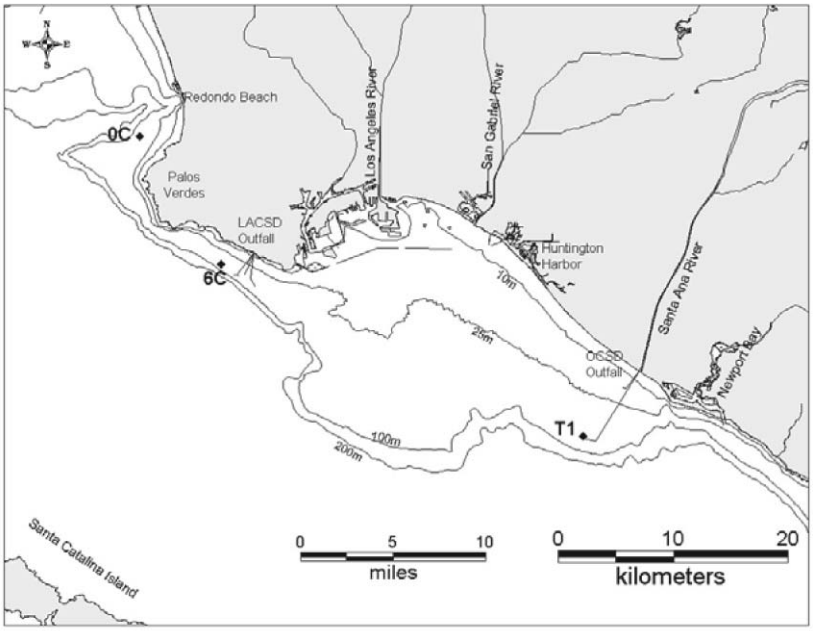

Figure 1. Map of the sampling locations off the coast of southern California. Stations 6C and T1 are adjacent to the outfalls of the Los Angeles County Sanitation District (LACSD) and the Orange County Sanitation District (OCSD), respectively.

METHODS

Construction of SPME Samplers

A typical SPME sampler consists of a 100-mm PDMS-coated fiber assembly (Part No. 57341-U; Supelco, Bellefonte, PA) and a 15 X 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. All SPME fibers were conditioned at 280°C under a helium stream for 1 h. The assembled SPME samplers were wrapped in aluminum foil and stored at –20 °C.

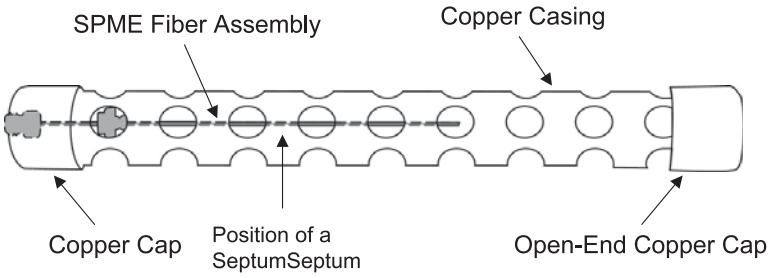

Figure 2. Schematic of the SPME-based sampling device.

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 Station 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 of deployment, each SPME sampler was carefully removed from the mooring and the fiber assembly was excised 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°C until analysis.

A parallel sampling employing the Infiltrex 100 system was conducted at Stations 6C and T1 (Figure 1). The operating procedures for this in-situ sampling method were the same as those employed in previous studies (Zeng *et al.* 1999, Zeng *et al.* 2002, Zeng and Tran 2002). One sample each was collected from Stations 6C and T1 with the volumes of water processed being 999 and 1,737 L, respectively.

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 (Zeng *et al.* (submitted)) 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 mm 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 mamps.

The SPME-based sampling method only measures organic chemicals in the dissolved phase, whereas the Infiltrex 100 system obtains both the particulate and dissolved phase (operationally defined as filtrates passing through a 0.7 mm glass fiber filter) materials. In this study, only the dissolved phase concentrations from both sampling methods were compared. Dissolved organics

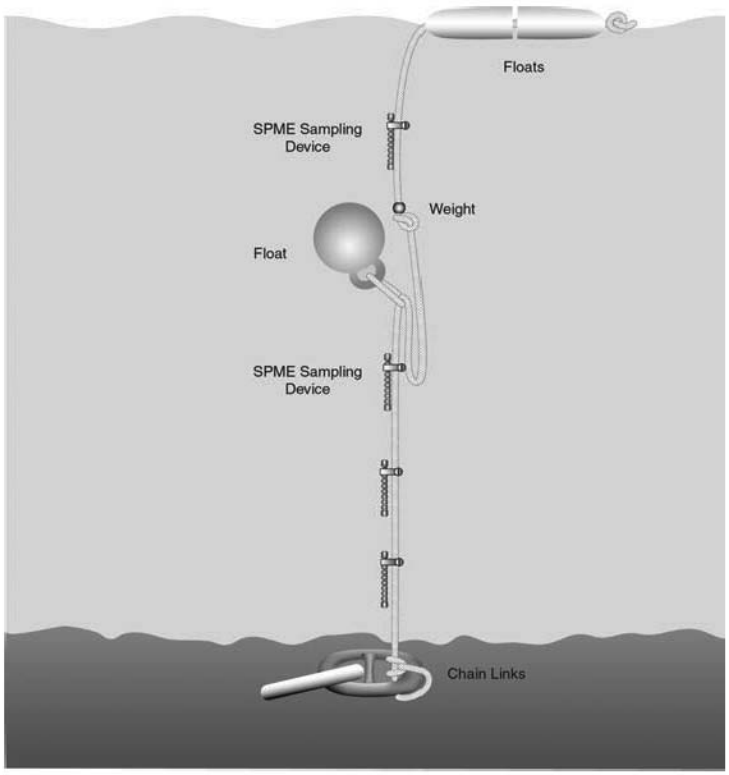

Figure 3. Schematic showing the field deployment of SPME samplers at various depths in the water column.

retained by the XAD-II resin-packed Teflon® columns were eluted and analyzed using the proce

dure described previously (Zeng *et al.* 1999). 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. Reporting limits were 0.050 and 0.029 ng/L for the 6C and T1 samples, respectively.

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) (Zeng and Noblet 2002):

$$N_f = \frac{K_f V_f (V_w + K'_H V_h)}{K_f V_f + V_w + K'_H V_h} C_w^0 \qquad (1)$$

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 is the dimensionless Henry's Law constant. In open oceans, $V_w \gg K_f V_f$ and . Therefore, Equation (1) can be simplified to:

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

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 GC-MS-1 defined elsewhere (Zeng *et al.* (submitted)); hence the $K_f V_f$ values determined with this instrument were used for quantitation. The reporting limits for the SPME samples were estimated from Equation (2), but N_f was set to the lowest calibration amount (0.025 ng) in the solvent-prepared standards and in this specific situation was designated as the reporting limit.

Results

Equilibrium Deployment Time

Deployment times were compared at all three sampling locations (Figure 1) at the 2 m and 10 m depths. The range of deployment times used for comparison was estimated from kinetic experiments reported elsewhere (Zeng *et al.* (submitted)) prior to field cruises. Equilibrium or near-equilibrium was achieved for all the target analytes with an extraction time of 12 d and an agitation velocity of ~4 cm/s, which is similar to the near-bottom current velocity (~5-6 cm/s) in southern California (Southern California Coastal Water Research Project 1994).

The results indicate that deployment times of 18 and 30 d yielded statistically identical concentrations of *p*,*p*'-DDE (Figure 4A) and *o*,*p*'-DDE (Figure 4B) at the 2 m and 10 m depths of Stations 6C and 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 m and 10 m depths for deployment times of 23 and 43 d (Figure 5). These comparisons suggest that equilibrium sampling by the SPME sam-

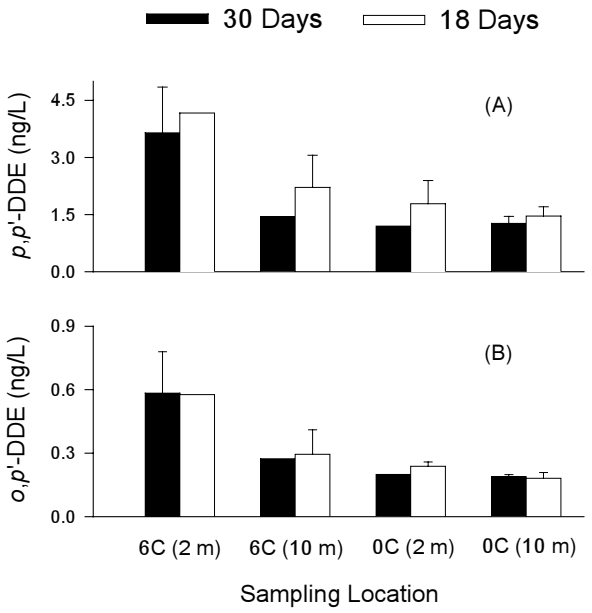

Figure 4. Water column concentrations of (A) p,p'-DDE and (B) o,p'-DDE obtained with SPME samplers for two timepoints at the 2 m and 10 m depths of Stations 6C and 0C (Figure 1). Sampling was conducted in May-June 2003.

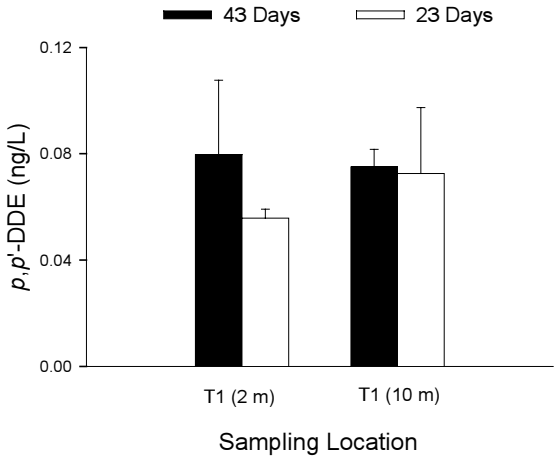

Figure 5. Water column concentrations of p,p'-DDE obtained with SPME samplers deployed for two timepoints at 2 m and 10 m depths of Station T1 (Figure 1). Sampling was conducted in June-July 2003.

plers 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 in-situ pump 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 all PCB congeners were not 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 only 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*'-DDE and DDD. The SPME samples contained detectable *o,p*'- and *p,p*'-DDE and *p,p*'-DDD, but non-detectable *o,p*'-DDD. This is again due to higher reporting limit (0.18 ngL) for *o,p*'-DDD with SPME samples than its concentration (0.090 ng/) 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 mass spectrum of *p,p*'-DDE from the SPME sample reasonably matched with that from the NIST reference library, in addition to a good agreement between the retention times for the SPME sample and the solvent-prepared standard analyzed prior to the sample analysis. Nevertheless, it is intended for qualitative assessment only.

Efficacy of the SPME-Based Sampling Method

The efficacy of SPME samplers was assessed against that of the Infiltrex 100 system deployed at the 2 m depth of Stations 6C and T1 (Figure 6). Results from two previous samplings (Zeng *et al.* 1999, Zeng and Tran 2002) using the Infiltrex 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.

Table 1. Comparison of dissolved phase concentrations (ng/L) of PCB congeners and chlorinated pesticides obtained with an Infiltrex 100 water pumping system and SPME samplers at the 2 m water depth of Stations 6C and T1 (Figure 1).

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

a --: 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 Station 6C and T1 pumping samples were 0.050 and 0.029 ng/L, respectively): 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); a-chlordane (0.12); g-chlordane (0.11); chlordene (0.068); chloropyrifos (0.91); diazinon (5.2); dieldrin (0.43); endrin (0.97); cis-nonachlor (0.16); trans-nonachlor (0.087); oxy-chlordane (0.086); o,p'-DDT (0.080); and p,p'-DDT (0.094). b 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

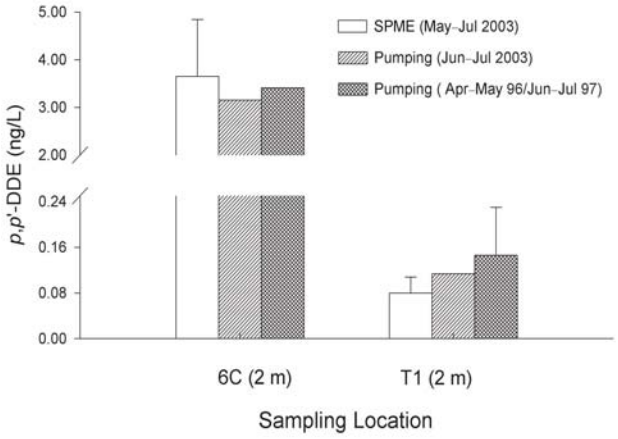

Figure 6. Water column concentrations of p,p'-DDE obtained with SPME samplers and an Infiltrex 100 water pumping system at the 2 m depth of Stations 6C and T1 (Figure 1).

Additional comparison between the SPME samplers and Infiltrex 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 essentially overlap with those obtained with the Infiltrex 100 system in June-July 1997 (Figure 7).

Discussion

This study, for the first time to the best of our knowledge, successfully employed a SPME-based method in sampling of 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. The efficacy of the SPME sampling method developed in this study was highly consistent with that of a large-volume sampling technique employing an Infiltrex 100 system (Figures 6 and 7). Comparing to the Infiltrex 100 system, the

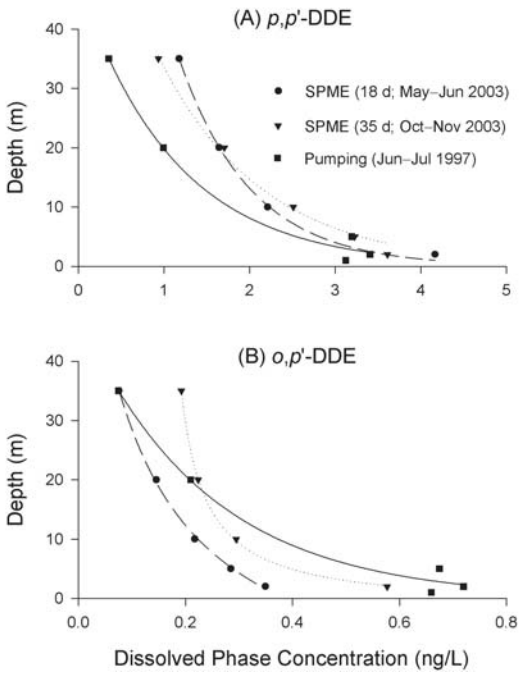

Figure 7. Water column vertical profiles of (A) p,p'-DDE and (B) o,p'-DDE at Station 6C (Figure 1) obtained with SPME samplers and an Infiltrex 100 water pumping system.

use of SPME samplers is clearly advantageous in two aspects. 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 Infiltrex 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 aspect 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-based sampling method with SPMD-based sampling approaches. The SPMD technology was first introduced by Huckins and co-workers (Huckins *et al.* 1990), and has since undergone extensive development (Petty *et al.* 2000, Lu *et al.* 2002). Triolein has been widely used as a sorbent phase in SPMDs 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 (Lu *et al.* 2002). SPMDs using PDMS and C_{18} Empore™ disk as sorbent phases have also been developed (Kingston *et al.* 2000, Vrana *et al.* 2002, Wennrich *et al.* 2003). In general, the detection capacity of SPMDs is superior over that of SPME samplers. This is apparently attributed to the much larger sorbent phase (generally ~1 mL) often employed in SPMDs than that (~0.6 µL for a 100 µm 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 from their correlation with K_{ow}s (Chiou 1985). On the other hand, the membrane design with SPMDs intrinsically results in considerably slow 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 (Gale 1998). By contrast, deployment time of ~18 d with SPME samplers appeared sufficient for equilibrium sampling of *p*,*p*'- and *o*,*p*'-DDE (Figures 4 and 5) with experimental log K_{ow} values in the range of 6-7 (DeBruijn *et al.* 1989). As a result of the slow kinetics with SPMDs, quantitation is usually performed under non-equilibrium situations. This requires accurate determination of sampling rates for specific chemicals on specific SPMDs. Furthermore, SPMD samples have to undergo extensive post-deployment treatment (e.g., solvent dialysis, cleanup, fractionation, and concentration) before they can be analyzed instrumentally. By contrast, the SPME samples acquired in the present study could be processed (thermal desorption and analysis) 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.

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 Equation (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 preferred to increase sorp-

tion capacity (assuming equilibrium extraction is achieved). However, a large sorbent phase may result in slow sorption kinetics, subjecting SPME samplers to extended deployment durations. 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. Amid the low cost of constructing and operating SPME samplers, use of multiple SPME samplers at each sampling point appears to be a feasible option to ensure the entirety of any sampling program.

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 7) indicate that sediments remain the main source of DDT compounds to the water column, a view originally derived from the 1997 sampling (Zeng *et al.* 1999) and subsequently subject to heated debates (Paulsen *et al.* 1999, Zeng and Tran 1999). Sediments on the Palos Verdes Shelf are known to contain high levels of DDTs (Stull *et al.* 1996, Venkatesan *et al.* 1996). 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 (Young *et al.* 1976, Lee 1994). This reduction has been hypothesized to occur via two routes. The first route is in-situ biodegradation (Quensen *et al.* 1998, Quensen *et al.* 2001) 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 (Eganhouse *et al.* 2000). The second route of the mass reduction is via physical processes, such as resuspension, dispersion, and advection, etc. (Zeng and Venkatesan 1999, Zeng *et al.* 1999). 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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