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SPME WITH PERFORMANCE REFERENCE COMPOUNDS FOR IN SITU MEASUREMENT OF DDT AND METABOLITES IN OCEAN WATER

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Introduction

The freely dissolved concentration (C_{free}) is a critical parameter for estimating bioavailability and assessing risks of persistent organic pollutants (POPs). A number of passive sampling techniques have been used for C_{free} measurement, which include semipermeable membrane devices, polyethylene devices (PED), polyoxymethylene, and solid-phase microextraction (SPME). These passive samplers all operate on the presumption of equilibrium partition between the sampler sorbent and water. However, many studies show that for strongly hydrophobic compounds, it may take several months or even longer to reach equilibrium.(1) This limitation is the largest technical barrier hampering the practical application of these samplers.

An effective approach to circumvent this limitation is to preload passive samplers with performance reference compounds (PRCs), ideally isotope labeled analogues of the target analytes.(2,3) This method is based on isotropic exchange between the native analytes and their isotope-labeled counterparts, where uptake of the target analytes into the sampler is estimated from the desorption of PRCs from the sampler, allowing for virtually in situ calibration during sampling.(2,3) To date, PRC calibration has been successfully applied in PED for in situ measurement of C_{free} of PAHs, PCBs, hexachlorobenzene, and DDTs. (4,5) However, the coupling of PRCs with SPME has not been adequately explored, especially for in situ monitoring. Here we report the development of PRC-SPME for in situ monitoring of DDT and metabolites in deep ocean above a historically contaminated sediment floor – the Palos Verdes Shelf (PVS) Superfund site (Figure 1). The PVS site is off the coast of Los Angeles, and is heavily contaminated with DDTs and PCBs due to decades of discharge of municipal and industrial wastewaters. Stable isotope labeled analogues were preloaded as PRCs onto disposable PDMS fibers and deployed to measure C_{free} of DDTs. The method performance was evaluated against other sampling approaches.

Materials and methods

Two types of fiber with different PDMS coating thicknesses, i.e., a thin-coating fiber (430-μm glass core with a 35-μm coating) and a thick-coating fiber (430-μm glass core with a 100-μm coating) (Polymicro Technologies, Phoenix, AZ) were used. All the fibers were cleaned and preloaded with PRCs as described in a previous study.(6) An assembly of the PRC-SPME passive sampler consisted of three 10-cm thin-coating PDMS fibers or one 10-cm thick-coating PDMS fiber in a 15×1.5 cm perforated copper casing.

Samplers were deployed at five locations (BA4C, BA7C, BA8C, BA9C, and W3) at the PVS Superfund site and at a background station (T11) approximately 24 km SE of the discharge point (Figure 1). Samplers were anchored by chain links and suspended at three depths for each station using a subsurface float: 5 m below the surface ("surface"), 5 m above the bottom ("bottom"), and 30 m below the surface ("mid-depth", except 100 m below the surface for W3 station). Samplers were retrieved 33 d after deployment.

The fibers were rinsed with deionized water, wiped with a damp paper towel to remove any visible particles, cut into 2-cm pieces and transferred into 7-mL scintillation vials. The fibers were then extracted twice with n-hexane by sonicating for 15 min. The combined extract was concentrated under nitrogen, and the residue in 100 μL hexane was spiked with ^{13}C-p,p'-DDD as the internal standard prior to analysis on a Varian 3800 GC-MS/MS.

Diffusive flux of DDTs in the water column from the bottom floor to upper surface can be estimated by Fick's first law of diffusion:

$$Flux = D_w/\delta(C_{bottom} - C_{surface})$$

where D_w is the compound's diffusion coefficient in water, δ is the boundary layer thickness, C_{bottom} and $C_{surface}$ are the freely dissolved concentrations at the sampling depths of bottom and upper surface, respectively. The D_w value for both o,p'- and p,p'-DDE is $4.23\times10{-10}$ m^2/s.

Results and discussion

Cfree of DDTs in Seawater: DDT metabolites DDE and DDD were successfully detected using the 35-μm and 100-μm PDMS fibers. The samplers with 35-μm PDMS fibers offered more accurate C_{free} measurements for DDE. Overall, the detected compounds were dominated by o,p'- and p,p'-DDE. The derived C_{free} for o,p'-DDE ranged from 14 pg/L near the surface at station BA9C to 750 pg/L in the bottom layer of water column at station BA8C, while that of p,p'-DDE ranged from 6 pg/L in the surface layer at station T11 to 2170 pg/L near the bottom at station BA8C. The highest C_{free} for o,p'-DDD was 24 pg/L at station W3 and for p,p'-DDD was 75 pg/L at station BA8C. Likely due to the very low concentrations, DDT in its parent form was not detected in any of the samplers, suggesting that DDT at this Superfund site had degraded extensively to its metabolites over many decades in the marine system. This chemical profile was in good agreement with previous surveys at this site in which DDE analogues were also identified at relatively high levels, followed by DDD.[5]

The concentration of detected compounds at the same sampling station increased vertically towards the bottom floor, indicating that the bed sediment acted as a source of these chemicals. Overall, the fluxes of o,p'- and p,p'-DDE in the water column from the bottom to upper surface followed the order BA8C > BA7C > BA4C > BA9C > W3 > T11. This pattern was consistent with previous studies showing that BA8C had the highest flux of DDTs from the sediment to water column.[7,8] The fluxes of o,p'- and p,p'-DDE in the water column from the bottom to upper surface at the contaminated site ranged from $3.8\times10{-6}$ to $7.67\times10{-5}$ ng/cm^2/yr (Table 1). In contrast, o,p'- and p,p'-DDE fluxes between sediment and water interface at the same site ranged from 42 to 1100 ng/cm^2/yr.[7] These fluxes validated again the directional transport of DDTs from the contaminated sediment to the overlaying water, and also implying enormous dilution once these contaminants moved into the water column.

Comparison with Other Sampling Methods. The C_{free}s derived by 35-μm PDMS fibers (with PRC calibration) in this study correlated closely with those measured using PRC-calibrated PED samplers deployed at 5 m off the bottom for 32 d at the same stations (BA4C, BA8C, and BA9C) in an earlier study.[5] These results suggest that C_{free}s measured by the two types of samplers can be converged by an appropriate correction factor. Overall, C_{free}s of DDE and DDD in this study were 0.8 to 3.8 times of those measured by PED sampler. The small difference may be attributed to uncertainties in the sampler and water partition coefficients used for C_{free} calculation. Taking the sensitivity and other experimental factors into consideration, the PRC-disposable PDMS fiber combines the advantages of PED and SPME. Compared with PED, the analysis of PDMS fibers consumes only a small volume of solvent (10 mL hexane, versus 900 mL dichloromethane), and also much smaller quantities of PRCs because of the extremely small volume of sorbent.

Application Considerations. This study clearly demonstrated the feasibility of coupling disposable PDMS fiber with PRCs for in situ environmental sampling of POPs such as DDTs. The use of PRCs allows for more accurate estimation of C_{free} prior to attaining equilibrium between the sampler and the sampled matrix. Even though a single time point (33 d after deployment) was used in this study, the principle of PRC-SPME is such that another time interval may be also used, as long as a significant fraction of the preloaded PRCs is desorbed from the sampler. This feature implies that the performance of PRC-SPME is not constrained by the time of sampler retrieval. The good conditions and full recovery of PDMS fibers after 33 d of exposure in the ocean suggest that this sampler may survive rough environmental conditions. By using different fiber lengths and preloaded PRCs, this sampling technique may be readily adapted for the in situ measurement of C_{free} of other POPs and in other aquatic environments.

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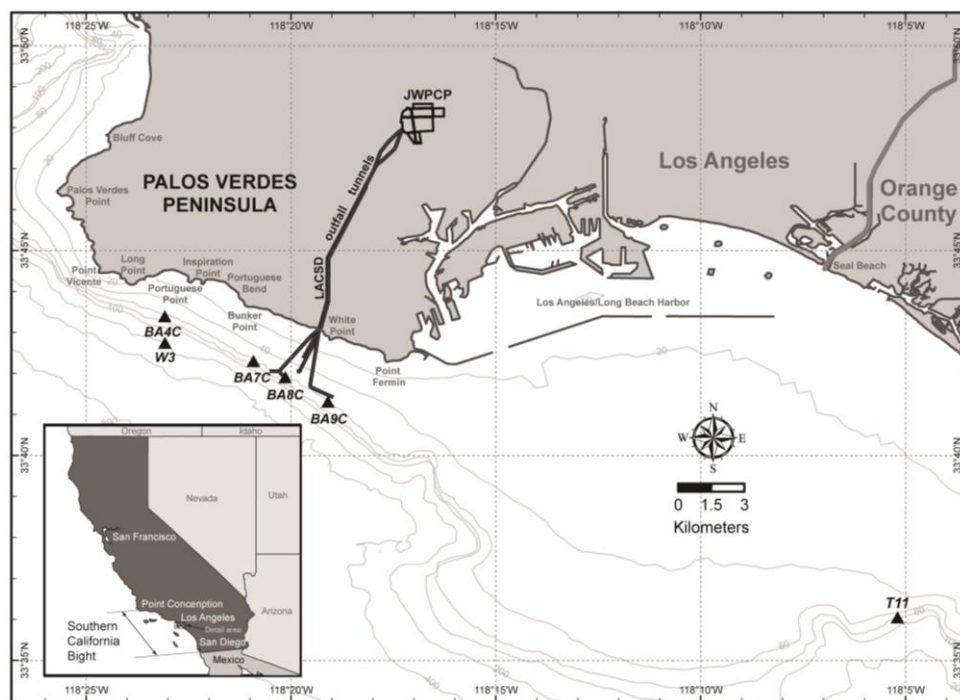
Figure 1. Map of sampling locations off Palos Verdes Shelf Superfund site off the coast of Los Angeles, California

Table 1. Fluxes ($\times 10^{-5}$ ng/cm^2/yr) from ocean floor to overlaying water

Compound	BA4C	BA7C	BA8C	BA9C	W3	T11
			Station location			
			Bottom to surface flux			
o,p'-DDE	1.18	1.48	1.82	0.50	0.38	-
p,p'-DDE	4.21	5.01	5.26	1.67	1.19	0.023
			Bottom to mid-depth flux			
o,p'-DDE	1.70	2.10	2.82	0.70	0.70	-
p,p'-DDE	6.10	6.61	7.67	2.18	2.13	0.025