

# Concentration and fate of persistent organochlorine pesticides in estuarine sediments using headspace solid-phase microextraction

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## Abstract

The concentration and fate of persistent organochlorine pesticides (OCPs) in estuarine surface sediments in Erh-jen and Lan-yang rivers, Taiwan were investigated using headspace solid-phase microextraction (HSSPME) method to evaluate the possible pollution potential and guideline for OCP concentrations in Taiwan. The HSSPME method exhibits a good analytical performance with low detection limits for OCP determination in sediment. In addition, results obtained using the developed HSSPME method were in good agreement with those obtained using Soxhlet extraction in a certified sample. The developed analytical method was further applied to the determination of concentrations of OCP residues in surface sediments from the estuaries of the selected rivers in Taiwan. A total of 20 surface sediments from each river was collected from 10 sampling stations. The total OCP concentrations in sediments from Erh-jen River ranged from 0.17 to 5.04 ng/g-dw with the mean values of 0.25–1.24 ng/g-dw for HCHs, 0.10–0.89 ng/g-dw for cyclodienes and 0.16–0.64 ng/g-dw for DDTs. The concentrations of OCPs in sediments from Lan-yang River were in the range 0.37–0.9 ng/g-dw with an average of lower than 0.5 ng/g-dw. HCHs and DDTs were abundant in the estuarine sediments from the selected rivers. Results obtained in this study show that the origin of OCPs in the surface sediments from Erh-jen River is a combination of erosion of the weathered soils and long-range atmospheric transport, while the OCP concentrations found in Lan-yang River could be regarded as the background levels of OCPs in Taiwan.

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**Keywords:** Headspace solid-phase microextraction (HSSPME); Surface sediments; Persistent organochlorine pesticides (OCPs); Fate

## 1. Introduction

The contamination of persistent organic pollutants (POPs) in the environments has become a global concern due to their carcinogenic and mutagenic properties.

Organochlorine pesticides (OCPs) have been extensively used in past decades against vegetal pests and vector-borne diseases, and have highly contaminated the soil and sediment environments. Several OCPs including HCHs, aldrin/dieldrin, endosulfan, and DDTs have been promulgated as POPs or endocrine disrupting chemicals (EDCs). Although OCPs have been officially banned for over 30 years, residues of OCPs also can be detected in foods, soils, sediments and biota (Willett

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et al., 1998; Doong and Lee, 1999; Doong et al., 2002a; Feng et al., 2003; Verweij et al., 2004). Recent work has depicted that the chlorinated pesticides could be found in the range 0.03–25.17 ng/g-dry weight (dw) in marine and river sediments (Sarkar et al., 1997; Doong et al., 2002b; Hartwell, 2004). In addition, some OCPs including DDTs, HCHs and endosulfan are still used in some countries around the tropic and sub-tropic belts for agricultural and medical purposes. These compounds can be deposited into the marine and river sediments through long-range atmospheric transport (LRT), and pose possible hazard to the human beings and ecosystems. Therefore, the determination of concentration and fate of OCP residues in sediments can provide crucial information on anthropogenic impact in the environments.

The traditional method for the analysis of OCPs in solid samples is usually comprised of three steps: extraction, clean-up and analysis. Soxhlet extraction with a conventional SPE adsorption column to remove impurities is a well-established standard method for the determination of OCPs in solid samples (Doong and Lee, 1999; Doong et al., 2002a). However, these procedures are usually expensive and both labor- and time-consuming because, in most cases, typical environmental samples cannot be directly analyzed by the chromatographic techniques. In addition, large amounts of sample volumes are usually needed because of the low concentrations of OCP residues in sediments. Therefore, the development of an efficient analytical technique with low detection limits is important to rapidly and accurately determine the concentrations of OCP residues in sediments.

Solid-phase microextraction (SPME) is a convenient and fast analytical technology, which has been widely accepted for the determination of volatile and semivolatile organic compounds in aqueous samples (Pawliszyn, 1997; Doong et al., 2000a; Popp et al., 2003). Several advantages such as cheap, solvent free, using whole sample for analysis, and easy to automate can be pointed out in relation to this technique when compared to the conventional method. An interlaboratory study on pesticides analysis by SPME was also carried out with participation of eleven laboratories worldwide (Gorecki et al., 1996). Results of the analysis showed that SPME was an accurate and fast method for sample preparation and analysis in aqueous solutions. In addition, head-space SPME (HSSPME) has been used to determine the spiked pesticides in soils (Ng et al., 1999; Doong and Liao, 2001), and polychlorinated biphenyls (PCBs) in soils and sediments (Hawthorne et al., 1998). To enhance the desorption efficiency of pollutants from environmental matrix and to increase the extraction efficiency of SPME fiber, the combination of microwave-assisted extraction with SPME method has been developed for the determination of OCPs in water (Cai et al., 2003; Li et al., 2003; Yan and Jen, 2004). In addition, the use of surfactant to enhance the extraction of

PAHs in soil (Doong et al., 2000b) and in a certified marine sediment (Pino et al., 2003) has been reported. However, the applicability of HSSPME to the determination of OCP residues in sediment samples still remains unclear.

In Taiwan, a broad spectrum of pesticides was used for agricultural activities as well as vector controls. HCH, endosulfan and DDT were extensively employed from the early 1950s for the control of soil-dwelling insects until the official ban commenced in 1974. It is estimated that  $2.5 \times 10^7$  kg of OCPs were released to the environments annually. Previous studies showed that there still exist a variety of OCP residues in the river and estuarine sediments in Taiwan (Doong et al., 2002a,b). The detected concentrations were 0.52–11.4 ng/g-dw for HCHs and 0.21–11.4 ng/g-dw for DDTs. However, there is no official guideline or regulations for OCPs in sediments in Taiwan, and the information on pollution potentials of OCPs in estuarine sediments is still limited.

In this study, the concentration and fate of persistent OCPs in estuarine surface sediments from the selected rivers in Taiwan was investigated using HSSPME method to evaluate the possible pollution potential and guideline for OCPs in Taiwan. The HSSPME method in relation to extraction temperature, adsorption time, and matrix effect was optimized. Erh-jen and Lan-yang rivers, located in southern and northeastern Taiwan, respectively, were selected to represent the highly polluted and unpolluted rivers. Moreover, ten OCP compounds including HCHs, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, and DDTs were selected as the model compounds because these compounds are promulgated as POPs and/or EDCs, which pose toxicity to the ecosystem.

## 2. Materials and methods

### 2.1. Reagents and Materials

Standard mixtures of OCPs at a concentration of 2000 µg/ml in toluene:hexane (1/1, v/v) and a 100-µm poly(dimethylsiloxane) (PDMS) fiber were purchased from Supelco Co., Inc. (Bellefonte, PA). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA). Triton X-100, sodium dodecyl sulfate (SDS), Brij 30, and Brij 35 were obtained from Sigma-Aldrich Co. (Milwaukee, WI). Tween 80 and cetyltrimethylammonium bromide (CTAB) were purchased from Merck Co. (Darmstadt, Germany).

### 2.2. Study area and sampling

The Erh-jen River is one of the most polluted rivers in Taiwan, which receives large amounts of industrial

wastewater and sewages. The average concentrations of dissolved oxygen (DO), biochemical oxygen demand (BOD<sub>5</sub>), and ammonium nitrogen (NH<sub>3</sub>-N) in water samples were 1.2, 17.8 and 12.1 mg/l, respectively. It has a catchment area of 350 km<sup>2</sup> and a total length of 65 km. The river has long historically contaminated with heavy metals, PCBs and PCDDs. The Lan-yang River, which located in a traditional agricultural production area in northeastern Taiwan, is a relatively unpolluted river in Taiwan. The catchment area and total length of Lan-yang River are 978 km<sup>2</sup> and 73 km, respectively.

Ten sampling sites near the outlet of each river were selected to understand the distribution of OCP concentrations in estuarine sediments from Erh-jen and Lan-yang rivers. The locations of the sampling sites in Erh-jen and Lan-yang rivers are illustrated in Fig. 1. A total of 20 surface sediment samples from each river was collected in April and September, 2002. The upper 15 cm of the surface sediments were sampled using a boat with a Birge–Ekman sediment grab sampler. Immediately after collection, sediments were preserved in deep freeze at –18 °C in order to avoid degradation.

### 2.3. Solid-phase microextraction procedures

The HSSPME extractions were performed by placing 0.5 g of spiked samples and 5 ml of deionized water into 15-ml amber vials capped with PTFE-coated septa. Sediments were sieved with a 20-mesh sieve to remove coarse particles and debris. Samples from Lan-yang River were prepared by spiking appropriate amounts of the diluted working solution (20 mg/l) to sediments to get the final OCP concentration of 4 ng/g-dw. Sediment samples were then shaken at 125 rpm to homogenize the OCPs and waited overnight to evaporate the solvent. Magnetic stirring with a 1-cm long Teflon coated stir bar was used to agitate the slurry at about 1000 rpm. The HSSPME experiment was conducted by immersing the fiber in the headspace of the sample with stirring the slurry for an appropriate time period, during which OCPs sorbed on the stationary phase of the fibers. After extraction, the fiber was thermally desorbed for 5 min into the glass liner of the GC injector at 270 °C. Possible carryover was removed by keeping the fiber in the injector for an additional period of time with the injector in the split mode. Reinserting the SPME fiber after the run showed no obvious carry over.

### 2.4. Analytical procedures

A Hewlett-Packard 5890 gas chromatograph (GC) equipped with an electron capture detector (ECD) was used for the experiments to determine the optimized SPME conditions and OCP concentrations in sediments. The carrier gas was nitrogen at a flow rate of 1.33 ml/min. The GC was operated in a splitless mode and the

splitless time was 5 min. The temperatures of injector and ECD were 250 and 280 °C, respectively. A 30-m PTE-5 capillary column (0.32 mm inner diameter, 0.25 μm film thickness, Supelco Co.) was used for separating OCPs. The column was held at 100 °C for 5 min, increased to 200 °C at a rate of 20 °C min<sup>-1</sup> for 3 min, and again ramped at 2 °C min<sup>-1</sup> to 230 °C, held for 1 min, and finally ramped to 250 °C at a rate of 4 °C min<sup>-1</sup>, and then held for 3 min. Nitrogen gas was used as the carrier and make-up gases at flow rate of 1.73 ml/min (linear velocity 25.2 cm/s) and 35 ml/min, respectively. Pentachloronitrobenzene and decachlorobiphenyl were used as the internal standards to confirm the retention times of OCPs.

The linearity of the method was tested by extracting seven aqueous standards with increasing concentrations over a range between 0.2 and 4 ng/g. The limit of detection (LOD) is defined as the concentration of an analyte in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The ECD response was calibrated by injecting liquid standards containing OCPs for calculating the total amounts sorbed by the fiber. The analyte recoveries were determined relative to the ratio of direct injection and the working standards prepared in hexane.

## 3. Results and discussion

### 3.1. Optimization of HSSPME

In order to develop an effective HSSPME procedure for the determination of OCP concentrations in sediments, extraction temperature, absorption time and the total amount of sediment were optimized. The change in temperature can influence the extraction efficiency of OCPs. Fig. 2 illustrates the signals of OCPs absorbed by a PDMS fiber with the extraction time of 60 min in the temperature range of 40–80 °C. In general, the increase in working temperature increased the extraction efficiency of OCPs, presumably due to the decrease in the partition coefficient ( $K_p$ ) between OCPs and sediment particles. Also, the elevated temperature significantly enhanced the mass transfer and diffusion rates of OCPs from solid phase to aqueous solution, and then to gaseous phase. Therefore, higher amounts of analytes were existed in the gaseous phase when the temperature increased. It is noted that the peak areas of DDTs became obvious when the temperature was higher than 70 °C. In addition, the absorption of analytes by the fiber is an exothermic process and a high temperature could decrease the SPME distribution coefficients ( $K_{SPME}$ ) of analytes (Santos et al., 1997; Doong and Liao, 2001), and the peak areas of HCH compounds ( $\alpha$ -HCH and  $\gamma$ -HCH) decreased when the temperature was higher than 60 °C. Since DDTs are major OCP compounds in Taiwan and HCHs still have sufficient

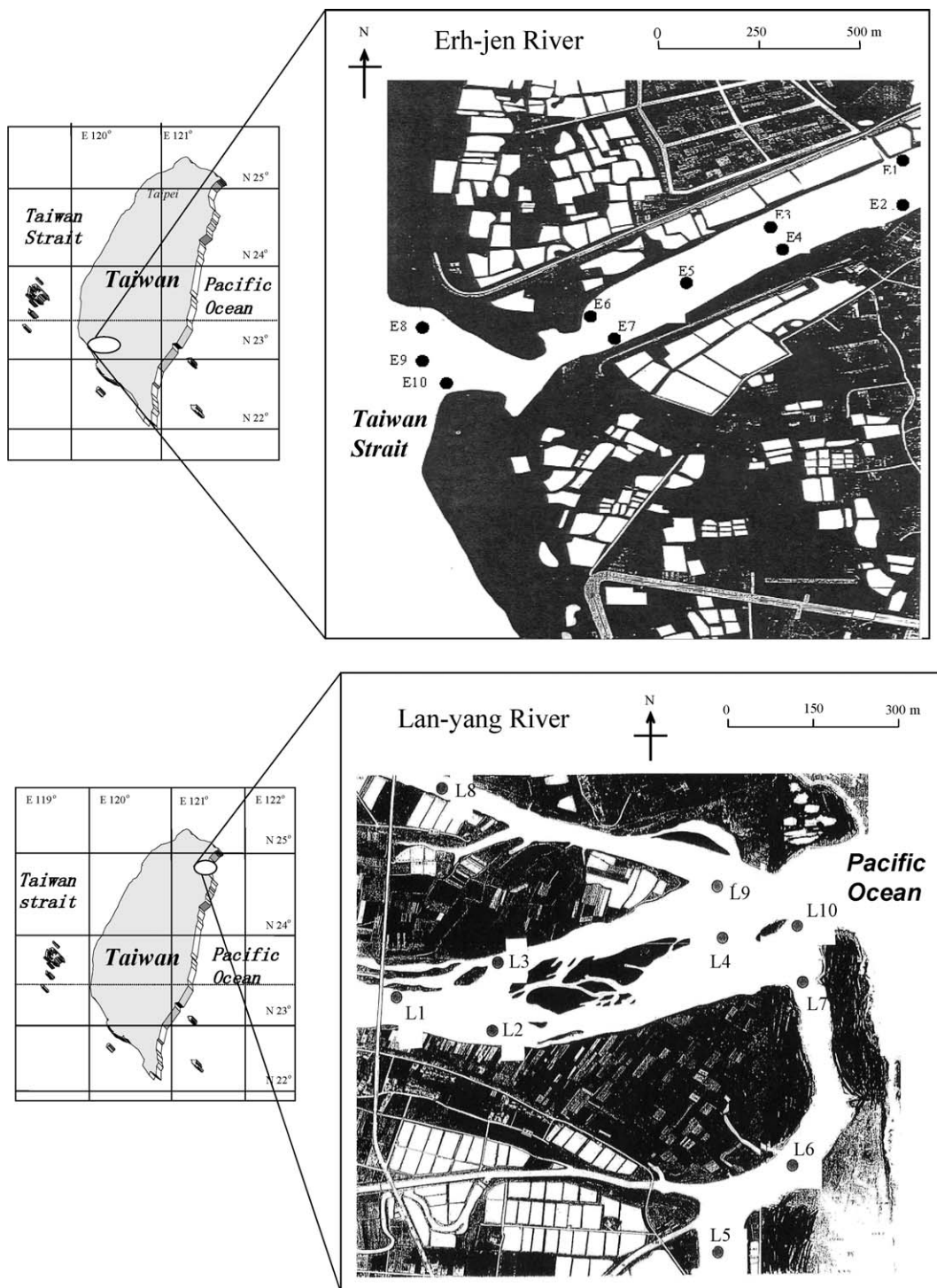


Fig. 1. The study areas and sampling locations in the Erh-jen and Lan yang rivers in Taiwan.

response at 70 °C, an extraction temperature of 70 °C was selected for further experiments.

The time required to reach the equilibrium between the fiber stationary phase and the sediment sample was

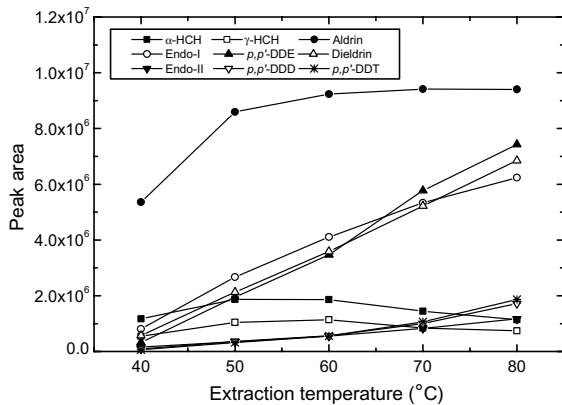


Fig. 2. The peak areas of organochlorine pesticides (OCPs) with a 100- $\mu$ m PDMS fiber at various temperatures ranging between 40 and 80 °C. The extraction time was 60 min.

determined at 70 °C. Fig. 3 illustrates the extraction time profiles of the OCPs. The equilibrium time ranged from 40 min for  $\alpha$ -HCH to 220 min for  $p,p'$ -DDT. The difference in responses was found to be dependent on the volatilities, distribution coefficients and structures of OCPs. The short equilibrium time for HCHs and aldrin may probably be due to the high vapor pressures at 70 °C (Doong and Liao, 2001). In addition, the low water solubilities and high  $K_{ow}$  values are the possible reasons for the long equilibrium time for DDT compounds. However, the equilibrium time of 220 min is too long for HSSPME procedures to extract OCPs. Also, the responses of several OCPs including endosulfan I, dieldrin, and HCHs decreased after 120 min. Therefore, an extraction time of 60 min was selected to perform the sample analysis.

The degree of partitioning of semivolatile organic compounds between the sediment and the headspace is generally low, and the total amounts of added sediments

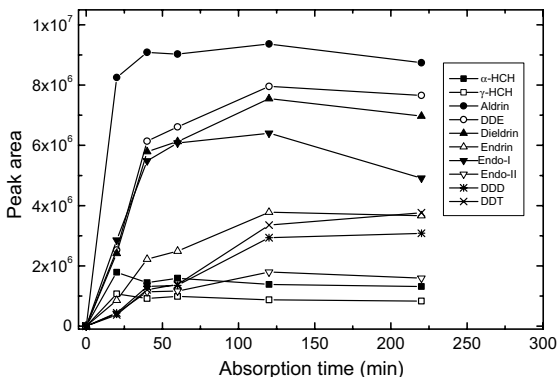


Fig. 3. The absorption time profiles of organochlorine pesticides (OCPs) with a 100- $\mu$ m PDMS fiber at 70 °C.

would influence the release rate of OCPs from the solid matrix. Therefore, various amounts of sediment ranging from 0.5 to 2 g were added into the vials containing 5 ml of water to understand the matrix effect of sediment on the extraction of OCPs. Fig. 4 shows the effect of sediment amount on the extraction of OCPs using the HSSPME at 70 °C. The response of OCPs decreased upon increasing amount of sediment, and 0.5 g of sediment showed highest response, clearly depicting the existence of matrix effect of sediment on OCP extraction. At high loading of sediment, the release of OCPs from sediment to water is hampered by the sediment matrix, and subsequently lowered the response of OCPs in headspace. SPME is an equilibrium extraction procedure and the extraction efficiency is dependent on the desorption rate of pollutants from sediments and the diffusion of pollutants. Mayer et al. (2000) depicted that the desorption was not the rate-limiting step for SPME extraction because the sediment has a substantially higher sorption capacity and a high exchange area relative to the fiber coating. Instead diffusion through the aqueous boundary layer near the fiber coating is considered the rate-limiting step. Since the turbulence level in the sediment was low and the viscosity was high which resulted in relatively thick unstirred boundary layers, time required for an equilibrium extraction of OCPs from solid sample to gaseous phase is long when the total amounts of added sediments were high. This result also means that only small amounts of solid sample is needed and sufficient for HSSPME analysis.

Several studies demonstrated that the addition of surfactant enhanced the apparent water solubilities of hydrophobic organic compounds sorbed on soils and sediments when the concentrations of surfactants exceeded their critical micellar concentrations (CMC) (Doong and Lei, 2003). A previous study also showed

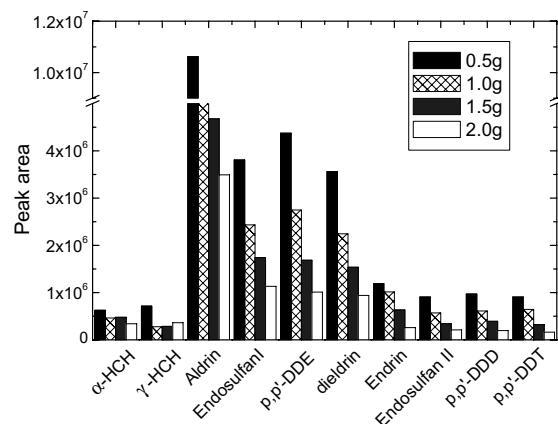


Fig. 4. Effect of sediment amounts on the extraction of OCPs with a 100- $\mu$ m PDMS fiber. The temperature and extraction time were 70 °C and 60 min, respectively.

that surfactants have various effects on the extraction efficiency of PAHs with HSSPME method (Doong et al., 2000b). In an attempt to enhance the extraction efficiency of OCPs from solid phase, especially HCHs and DDTs, six surfactants including Triton X-100, Tween 80, Brij 30, Brij 35, SDS, and CTAB were used. The concentrations of surfactants used were at  $1 \times$  CMC values. Fig. 5 shows the peak areas of OCPs in the presence of surfactants. Addition of SDS and CTAB significantly lowered the extraction efficiency of OCPs, presumably due to their ionic characteristics. The enhanced effects of nonionic surfactants on OCP extraction are compound-dependent. In general, Tween 80 and Brij 35 had the higher enhanced effect on the extraction of OCPs than those of Triton X-100 and Brij 30. This difference is mainly attributed to the different numbers of polyoxyethylene (POE) chain of the surfactants. The POE numbers of Brij 30, Triton X-100, Tween 80, and Brij 35 are 4, 10, 20, and 23, respectively, clearly

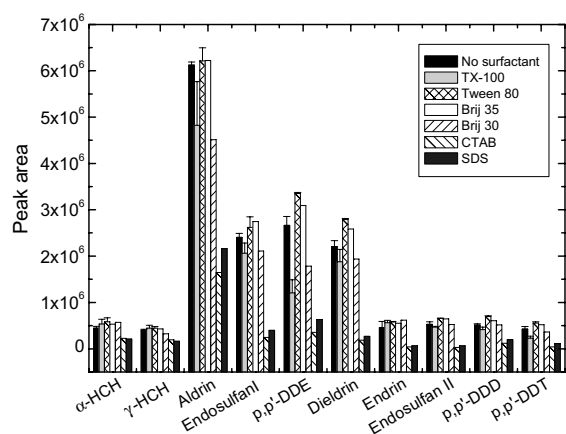


Fig. 5. Effect of surfactants on the extraction of OCPs with a 100- $\mu$ m PDMS fiber. The concentrations of surfactants were  $1 \times$  CMC.

showing that surfactants with long POE chain have higher capacity in enhancing the extraction of OCPs in sediments. In addition, the enhanced ratios for HCHs and DDTs extraction were 1.11–1.31 and 1.26–1.36, respectively, in the presence of Tween 80, while only 6–19% and 17–22% of the extraction efficiency were enhanced when Brij 35 was added. Therefore, Tween 80 was selected to enhance the sensitivity of HCHs and DDTs in real sample analysis.

### 3.2. Analytical performance

Table 1 shows the linear range, linearity, precision and limits of detection (LODs) of OCPs using the developed HSSPME procedure. The HSSPME procedure showed a good linear behavior in the tested range with correlation coefficients ranging between 0.988 to 0.998. The precision of the HSSPME procedure was determined by performing seven consecutive extractions and the relative standard deviations (RSD) were in the range of 3.7–9.6%. In addition, the limits of detection (LODs) ranged from 0.029 to 0.301 ng/g, which is much lower than the reported values obtained from Soxhlet extraction (Doong et al., 2002a) and the detection limits reported by US Environmental Protection Agency (EPA) Method 8081 (1.1–5.7 ng/g). This may probably be attributed to that SPME is a whole sample extraction procedure, while only a small fraction of the extract ( $\sim 1 \mu$ l) is analyzed in Soxhlet extraction.

Soxhlet extraction of OCPs in a certified CRM804-050 sample was used to validate the HSSPME procedure. Table 2 shows the recoveries of OCPs using HSSPME and Soxhlet extraction. Due to the high concentrations of OCPs in CRM soil, 0.02 g of CRM was used and mixed with unspiked sediments from Lan-yang River to get the total weight of 0.5 g. The mean values obtained by Soxhlet extraction and certified values of OCPs in CRM samples were also given. In general, results obtained with HSSPME agreed with the mean values obtained using Soxhlet extraction. The recoveries

Table 1  
The linear range, linearity, precision and limits of detection (LODs) of OCPs

Pesticides	Linear range (ng/g)	Linearity	Precision ( $n = 7$ )	LODs (ng/g)
$\alpha$ -HCH	0.2–4.0	0.988	5.4	0.064
$\gamma$ -HCH	0.3–4.0	0.989	7.8	0.301
Aldrin	0.3–4.0	0.997	3.7	0.029
Endosulfan I	0.3–4.0	0.998	4.4	0.036
$p,p'$ -DDE	0.2–4.0	0.998	3.7	0.054
Dieldrin	0.2–4.0	0.998	4.5	0.037
Endrin	0.3–4.0	0.998	5.6	0.034
Endosulfan II	0.2–4.0	0.998	6.4	0.084
$p,p'$ -DDD	0.2–4.0	0.997	9.6	0.082
$p,p'$ -DDT	0.2–4.0	0.997	9.1	0.072

Table 2  
Analysis of OCPs in CRM 804-050 sample using HSSPME and Soxhlet extraction procedures

OCPs	Certified value ( $\mu\text{g}/\text{kg}$ )	Recovery (%)	
		Headspace SPME	Soxhlet extraction
$\gamma$ -HCH	491.6	121 $\pm$ 7	82 $\pm$ 8
Aldrin	18.04	91 $\pm$ 13	92 $\pm$ 7
Endosulfan I	1464.3	74 $\pm$ 4	70 $\pm$ 9
<i>p,p'</i> -DDE	1519.6	71 $\pm$ 2	88 $\pm$ 8
Dieldrin	1862.5	81 $\pm$ 1	96 $\pm$ 9
Endrin	62.2	115 $\pm$ 14	120 $\pm$ 13
Endosulfan II	1128.2	96 $\pm$ 6	82 $\pm$ 7
<i>p,p'</i> -DDD	1530.6	95 $\pm$ 15	98 $\pm$ 5
<i>p,p'</i> -DDT	1060.1	94 $\pm$ 9	107 $\pm$ 8

Table 3  
Detected concentrations of OCPs in sediments from Erh-jen and Lan-yang rivers using the developed HSSPME method

Pesticides	Erh-jen River		Lan-yang River	
	Range (ng/g-dw)	Mean (ng/g-dw)	Range (ng/g-dw)	Mean (ng/g-dw)
$\alpha$ -HCH	0.14–1.07	0.33	0.16–0.61	0.26
$\beta$ -HCH	0.33–3.16	1.24	0.37–0.80	0.59
$\gamma$ -HCH	0.13–0.52	0.25	0.16	0.16
Aldrin	0.18–0.44	0.32	0.04	0.04
Endosulfan I	0.07–0.19	0.10	0.08–0.49	0.14
Dieldrin	0.09–2.31	0.89	ND	ND
Endrin	0.34–0.37	0.35	0.16	0.16
Endosulfan II	0.08–2.77	0.57	ND	ND
<i>p,p'</i> -DDE	0.14–0.22	0.17	0.17–0.26	0.23
<i>p,p'</i> -DDD	0.16	0.16	ND	ND
<i>p,p'</i> -DDT	0.15–1.12	0.64	0.45–0.74	0.69

ND: not detected.

of OCPs were 71–121% and 70–120% for HSSPME and Soxhlet extraction, respectively, showing that no significant difference in OCP concentrations between SPME and Soxhlet extraction with CRM mean values were observed. These results indicate that HSSPME can be considered as an alternative for the determination of OCPs in sediment samples.

### 3.3. Application to real sample determination

The distribution and fate of OCP residues in surface sediments from Erh-jen and Lan-yang rivers were determined using the developed HSSPME method. Table 3 shows the detected concentrations of OCP residues in sediments. The detected concentrations of OCPs in surface sediments from Erh-jen River were 0.14–1.07 ng/g-dw for  $\alpha$ -HCH, 0.13–0.52 ng/g-dw for  $\gamma$ -HCH, 0.18–0.44 ng/g-dw for aldrin, 0.14–0.22 ng/g-dw for *p,p'*-DDE, 0.09–2.31 ng/g-dw for dieldrin, 0.08–2.77 ng/g-dw for endosulfan II, 0.34–0.37 ng/g-dw for endrin, 0.16 ng/g-dw for *p,p'*-DDD, and 0.15–1.12 ng/g-dw for *p,p'*-DDT. The mean concentrations were 0.25–

1.24 ng/g-dw for HCHs, 0.10–0.89 ng/g-dw for cyclodienes and 0.16–0.64 ng/g-dw for DDTs. Doong et al. (2002a) investigated the distribution and fate of OCPs in surface sediments from Erh-jen River collected from October 1997 to April 1998, and found that HCHs and DDTs were the main OCPs in surface sediments. The total OCP concentrations detected in 1997 ranged between 0.57 and 23.67 ng/g-dw, which is higher than the concentrations found in this study (0.17–5.04 ng/g-dw). Since Erh-jen River is located in a strong agricultural sector in Taiwan, this result shows that the contamination of OCPs in Erh-jen River is mainly from the erosion of weathered soils and there is no new pollution sources existed in the riverine regions. Concentrations of OCPs in surface sediments from Lan-yang River were lower than those from Erh-jen River. The detected total OCP concentrations were in the range 0.37–0.90 ng/g-dw with the mean values of 0.16–0.59 ng/g-dw for HCHs, 0.04–0.16 ng/g-dw for cyclodienes and 0.23–0.69 ng/g-dw for DDTs.

Fig. 6 shows the total OCP concentrations at different sampling sites in the estuaries of Erh-jen and

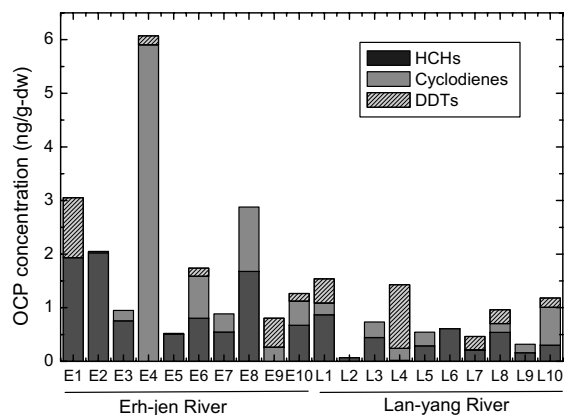


Fig. 6. The total concentration profiles of OCPs at different sampling locations in Erh-jen and Lan-yang rivers. The OCP concentrations were the sum of two sampling times.

Lan-yang rivers. In general, the detected concentrations of OCPs from each sampling site in Erh-jen River are higher than those found in Lan-yang River. The highest concentration was detected at sampling location E4 in Erh-jen River, presumably due to that E4 is located in the downstream of a wastewater treatment plant (WWTP). For Lan-yang River, the total OCP concentrations in sampling locations were, in general, lower than 1 ng/g-dw, which can be assigned as an unpolluted river in Taiwan. Lan-yang River is mainly used for agricultural and water supply purposes in northeastern Taiwan. Although this river receives massive sewage discharged from I-lan County, Taiwan, the averaged aqueous DO, BOD<sub>5</sub> and NH<sub>3</sub>-N concentrations in Lan-yang River are 7.8, 1.6 and 0.24 mg/l, respectively, which confirm that Lan-yang River is unpolluted. It is noted that the detected total OCP concentrations in sediments from Lan-yang River is comparable to the levels found in the Greenland sediments and Arctic region (<1–2 ng/g-dw) (Cleemann et al., 2000). This suggests that the contamination levels of OCPs found in Lan-yang River could be regard as the guideline for OCP levels in Taiwan.

Fig. 7 shows the detection frequency of OCPs in sediments collected from Erh-jen and Lan-yang rivers. Among the OCPs detected in Erh-jen River,  $\alpha$ -HCH was the most often found compound in sediment (50%), followed by  $\beta$ -HCH (30%),  $\gamma$ -HCH (30%), endosulfan II (30%) and *p,p'*-DDE (25%). This result clearly shows that HCHs are the most dominant compounds in estuarine sediments from Erh-jen River. Similar to the results in Erh-jen River, high detection frequency of  $\alpha$ -HCH (35%), *p,p'*-DDE (20%) and endosulfan I (20%) were observed in the estuarine sediments from Lan-yang River. It is noted that the detected frequencies of OCPs in sediments from Lan-yang River are also lower than

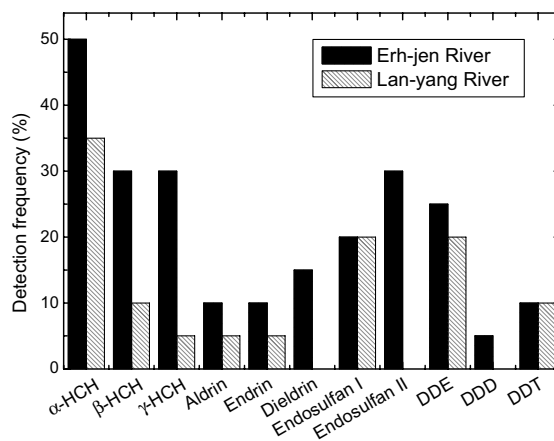


Fig. 7. The detection frequency of OCPs in sediments collected from Erh-jen and Lan-yang rivers. ND: not detected.

those from Erh-jen River. Several studies depicted that the contamination of hydrophobic organic compounds in sediments is dependent on the chemical properties of pollutants and the organic contents of sediments (McKenzie-Smith et al., 1994; Glynn et al., 1995). In this study, the total organic carbons (TOC) in water samples were  $6.28 \pm 0.92$  mg/l for Erh-jen River and  $1.11 \pm 0.62$  mg/l for Lan-yang River. A similar distribution pattern of volatile suspended solids (VSS) in sediment particles was observed. The VSS contents in sediments from Erh-jen and Lan-yang rivers were  $49.4 \pm 18.7$  and  $38.6 \pm 12.8$  mg/g, respectively, which is in accordance with the results of OCP concentrations obtained in this study.

The high detection frequency of HCHs in sediments shown in this study depicts that the contamination of HCH was widespread in Taiwan rivers. Recent studies also show that the contamination of HCH isomers is a serious problem worldwide (Fellin et al., 1996; Sarkar et al., 1997; Hong et al., 1999; Walker et al., 1999). Technical-grade HCH consists principally of five isomers,  $\alpha$ -HCH (60–70%),  $\beta$ -HCH (5–12%),  $\gamma$ -HCH (10–15%),  $\delta$ -HCH (6–10%) and  $\epsilon$ -HCH (3–4%) (Walker et al., 1999). The most often found isomers in the environment are  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers.  $\alpha$ -HCH was found to be the dominant compound of HCH in the estuarine sediments from the selected rivers in this study, suggesting that the contamination of  $\alpha$ -HCH may be attributed to the long distance transport from other areas. Some OCPs such as endosulfan and HCH are still used in some developing countries around the tropical belt and may be transported through the atmosphere and gradually deposited in the river at higher latitudes. Oehme et al. (1996) measured the seasonal concentration changes of organochlorines in the European Arctic and found that long-range atmospheric transport from more polluted



areas might lead to a significant concentration change in the Arctic air. It is estimated that the total global usage of technical grade HCH between 1948 and 1997 was around 10 million tons (Li, 1999). Among the HCH isomers,  $\alpha$ -HCH is more likely to partition to the air and transport for a long distance. These results depict that  $\alpha$ -HCH may be mainly from the long-range transport (LRT).

#### 4. Conclusions

In this study, headspace SPME method has been developed to effectively determine the concentration distribution and fate of OCPs in river sediments. The developed HSSPME method exhibits a good analytical performance with low detection limits for the determination of OCPs in estuarine sediments. In addition, the concentration of OCP residues in surface sediment collected from Erh-jen and Lan-yang rivers ranged from 0.17 to 5.04 ng/g-dw and from 0.37 to 0.90 ng/g-dw, respectively. HCHs and DDTs were found to be the most frequent detected compounds in the sediments from the selected rivers. The origin of OCPs in the surface sediments from Erh-jen River is a combination of erosion of weathered soils and long-range atmospheric transport, while the OCP levels found in Lan-yang River could be regarded as the guideline for OCP residues in Taiwan.

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