Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1068 (2005) 221–228
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Analysis of persistent organic pollutants in marine sediments using a novel microwave assisted solvent extraction and liquid-phase microextraction technique

Chanbasha Basheer [a], Jeffrey Philip Obbard [b], Hian Kee Lee [a, *]

[a] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore*
[b] *Tropical Marine Science Institute, National University of Singapore, 14 Kent Ridge Road, Singapore 119223, Singapore*

Received 30 September 2004; received in revised form 27 January 2005; accepted 31 January 2005

Abstract

A simple and novel analytical method for quantifying persistent organic pollutants (POPs) in marine sediments has been developed using microwave assisted solvent extraction (MASE) and liquid-phase microextraction (LPME) using hollow fibre membrane (HFM). POPs studied included twelve organochlorine pesticides (OCP) and eight polychlorinated biphenyl (PCB) congeners. MASE was used for the extraction of POPs from 1 g of sediment using 10 ml of ultrapure water at 600 W for 20 min at 80 °C. The extract was subsequently subjected to a single step LPME–HFM cleanup and enrichment procedure. Recovery varied between 73 and 111% for OCPs; and 86–110% for PCBs, and exceeded levels achieved for conventional multi-step Soxhlet extraction coupled with solid-phase extraction. The method detection limit for each POP analyte ranged from 0.07 to 0.70 ng g^{-1}, and peak areas were proportional to analyte concentrations in the range of 5–500 ng g^{-1}. Relative standard deviations of less than 20% was obtained, based on triplicate sample analysis. The optimized technique was successfully applied to POP analysis of marine sediments collected from the northeastern and southwestern areas of Singapore's coastal environment.

Keywords: Liquid-phase microextraction; Hollow fibre membrane; Persistent organic pollutants; Sediment analysis

1. Introduction

There is growing evidence that xenobiotic chemicals in the environment have the potential to elicit endocrine disruption in biota by impacting upon reproductive and hormonal functions [1]. Although these effects are not restricted to persistent organic pollutants (POPs) alone, these compounds are an important component of the range of xenobiotic chemicals now ubiquitous in the global environment [2–4]. Chlorinated organic compounds have a wide range of industrial and agricultural applications, and include organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethane (DDT) and Lindane (γ-HCH; hexachlorocyclohexane (HCH)), as well as the polychlorinated biphenyls (PCBs). Moreover, these compounds are chemically and biologically recalcitrant and readily undergo bioaccumulation in both terrestrial and aquatic organisms [5,6]. Introduction of these compounds into the marine environment via atmospheric deposition, oil spillages and sewage discharges results in their biomagnification in the food chain, ultimately posing a risk to human health [7]. Indeed, POPs are now routinely detected in fish and wildlife, as well as human adipose tissue, blood and breast milk [8,9].

The quantification of POPs in marine sediments can be achieved via several established methods. For example, USEPA method 3540 (Soxhlet extraction) has been used for extracting semi-volatile organic pollutants from sediments, as well as soils and solid wastes. In recent years, new extraction procedures have been developed for POPs in sediment samples. Supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) [10–12] and microwave assisted solvent extraction (MASE) [13,14] have all have been used. These techniques have allowed sample size and solvent

* Corresponding author. Tel.: +65 6874 2995; fax: +65 6779 1691.
E-mail address: chmleehk@nus.edu.sg (H.K. Lee).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.01.099

volume to be reduced, analytical precision to be improved. The main advantage of MASE is that it provides faster and more efficient sample extraction due to direct heat transfer by ionic conduction and dipole rotation.

Non-polar solvents do not absorb microwave energy. Therefore, in MASE, such solvents have poor extraction efficiencies compared to polar solvents or mixtures of solvents at least one of which must polar [15]. Addition of water (which is polar) improves the recoveries of the target analytes [16] as it facilitates non-polar organic solvents to absorb the microwave energy, and also enhances the release of analytes from the sample matrix [17]. Recently, water has been used as an alternative solvent as it is cost effective, safe and environmentally benign. As water has a higher permittivity (ε) and heat of vaporization (ΔH_v (kJ mol^{-1}), (78.3 and 46.0 at 25 °C) compared to organic solvents such as acetone (20.7 and 31.9 at 25 °C), hexane:acetone mixtures (1.9 and 31.9 at 20 °C) and methanol (32.6 and 37.5 at 20 °C), respectively [18], it is suitable for many polar analytes and has a better extraction efficiency than organic solvents during microwave extraction [19]. Moreover, after MASE with solvent, a clean-up step is required due to co-extraction of matrix materials with the solvent, thereby resulting in interferences during chromatographic separation [20,21].

Various types of solid phase extraction (SPE) cartridges have been used for sample clean up which includes C18, silica or ion exchange materials [22–24] that depend upon moderate to large amounts of solvent. Solid phase microextraction (SPME), a solventless extraction technique coupled to MASE has also been developed, although it is not widely deployed (in most cases, microwave digested samples were extracted using HS-SPME, and this reduces the sensitivity for semi- or nonvolatile analytes) as the fibers used are prohibitively expensive and subject to analyte carryover [25].

To overcome these shortcomings, we have developed a simple liquid-phase microextraction (LPME) cleanup and enrichment procedure supported by porous polypropylene hollow fiber membrane (HFM). HFM has already been shown to be effective for the enrichment and cleanup of various analytes in different media [26], including water, slurry [27], human urine, and plasma [28–30]. Recently, LPME has been successfully applied to soil samples by direct immersion-LPME [31] and headspace-LPME [32]. In this study we develop a MASE procedure coupled with LPME using HFM for cleanup, enrichment and extraction of POPs (i.e. OCPs and PCBs) from marine sediment samples. The new method was then applied to the analysis of POPs in marine sediments collected from Singapore's coastal marine environment.

2. Experimental section

2.1. Standard and reagents

HPLC grade solvents were purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system (Millipore, Milford, MA, USA). All pesticides used were purchased from Poly Science (Niles, IL, USA). A mixed stock solution containing twelve OCPs (i.e. α-HCH, β-HCH, Lindane, Heptachlor, Aldrin, Dieldrin, Endrin, Endosulfan, *p,p′*-dichlorodiphenyldichloroethane (*p,p′*-DDD), *p,p′*-DDT, Endrin aldehyde and Methoxychlor) and eight PCB congeners (i.e. 2-dichlorobiphenyl (CB-1), 2,3-dichlorobiphenyl (CB-5), 2,4,5-trichlorobiphenyl (CB-29), 2,2′,4,4′-tetrachlorobiphenyl (CB-47), 2,2′,3′,4,6-pentachlorbiphenyl (CB-98), 2,2',4,4',5,6'-hexachlorobiphenyl (CB-154), 2,2′,3,3′,4,4′,6-heptachlorobiphenyl (CB-171), 2,2′,3,3′, 4,5′,6,6′-octachlorobiphenyl (CB-200)) were obtained form Aldrich (Milwaukee, WI, USA).

A working standard solution of 1 μg ml^{-1} per OCP or PCB analyte was prepared by stock dilution in acetone. Oasis-HLB SPE cartridges were purchased from Waters (Milford, MA, USA). A MARS (CEM, Matthews, NC, USA) microwave extraction system (maximum power: 1200 W) was used for POP extraction from sediment. Accurel Q3/2 polypropylene HFM was purchased from Membrana GmbH (Wuppertal, Germany) and used in conjugation with a 10 μl micro syringe (needle tip 0.46 mm O.D.) purchased from Hamilton, Reno, NV, USA. The inner diameter of the HFM was 600 μm, wall thickness 200 μm and pore size 0.2 μm.

2.2. Sediment preparation

Solvent-washed blank sediment sample (pH 6 and total organic content 1.8%) was prepared using our previous procedure [33] and tested for POP analysis using Soxhlet extraction and no target analytes were detected. Several of the sediment samples were prepared by spiking appropriate amounts of the diluted working standards solutions to get final concentrations of 5–500 ng g^{-1} sediment. The sediments were first homogenized by hand mixing for ∼2 min and afterwards in a mechanical shaker while they were left for at least 4 h at room temperature to fully evaporate the solvent. Real sediment sampling was conducted from three locations in the northeastern and southwestern regions of Singapore's coastal environment. Sampling locations were all within 1 km of the busy industrial and shipping lane of the coastline. Surface sediments were collected using a Van Veen grab (1000 cm^2 sampling area). The samples were first air dried to constant mass at room temperature and then sieved through a screen (pore size 2 mm I.D.) to remove rocks, coarse particles and other large debris. A portion of the sediments were analysed using Soxhlet extraction prior to spiking. The pH value and organic content of the sediments were 8.2 and 4.6%, respectively.

2.3. MASE–LPME–HFM extraction

A 1 g sample of sediment was subjected to microwave heating with 8 ml of ultrapure water at 600 W. Water was the solvent used for MASE as it has high dielectric constant (i.e.78.3 ϵ), dipole movement, (i.e. 2.3), dissipation factor, (i.e. 1570 tan $\delta \times 10^{-4}$) and boiling point compared to

commonly used organic solvents [15]. After MASE, the extract containing POPs was transferred to a 10 ml volumetric flask. Sediments were further rinsed with 2 ml ultrapure water and the rinsate was then transferred to the same 10 ml volumetric flask. A 10 μl syringe with a cone-tipped needle (Hamilton, Reno, NV, USA) was used for the enrichment and extraction procedure. Solvent selection is an important aspect of LPME, where the solvent for analyte enrichment should be immiscible with water, have a low solubility and be compatible with the hydrophobic HFM. Based on our previous evaluation [34], toluene was selected. 5 μl of toluene was drawn into the syringe and the needle was tightly fitted to a 1.3-cm length of HFM that was previously heat-sealed at the other end. The HFM was impregnated with toluene for 10 s to dilate the membrane pores. The syringe needle-HFM was then immersed 5 mm below the surface of the sample solution which was agitated using a magnetic stirrer at 73 rad s^{-1} (700 rpm). The syringe plunger was depressed completely so that toluene completely filled the HFM. The syringe and 10 ml volumetric flask was held in place by clamps. Extraction between the toluene within the HFM and the sample solution was allowed to proceed, allowing the analytes to diffuse though the porous membrane and dissolve into the toluene. After the mass transfer of analytes from the aqueous sample solution to the organic phase, the magnetic stirrer was switched off and the toluene in the HFM was withdrawn into the syringe, which was then removed from the sample solution. The HFM was removed and discarded. 2 μl of the extract was injected into the GC–MS.

2.4. Soxhlet extraction and SPE

Marine sediment samples were extracted with the developed MASE–LPME–HFM procedure and compared with the well-established Soxhlet (USEPA 3540) method followed by SPE clean-up on an uncontaminated sediment. 5 g of uncontaminated sediment was spiked with 100 ng g^{-1} of each individual compound and placed into a thimble filter, prior to Soxhlet extraction with 250 ml of an acetone–hexane solvent mixture (1:1) for 12 h. After extraction, the extract was preconcentrated to 5 ml on a rotary evaporator at room temperature, and then subjected to clean-up with an Oasis-HLB SPE cartridge (Oasis-HLB was conditioned with a methanol:water (1:5) mixture; after loading, the sample was washed with 5% methanol in water and the POPs were eluted with methanol). Finally, the extract was pre-concentrated with a gentle steam of nitrogen and made up to 2 ml in a volumetric flask with acetone. 2 μl of extract was then injected into the GC–MS. For Soxhlet extraction with SPE-clean up, a separate calibration was used to calculate the exhaustive recoveries.

2.5. GC–MS analysis conditions

Sample analysis was carried out using a Shimadzu (Tokyo, Japan) QP5050 GC–MS equipped with a Shimadzu AOC–20i auto sampler and a DB-5 fused silica capillary column (30 m × 0.32 mm I.D., film thickness 0.25 μm, J & W Scientific, Folsom, CA, USA). Helium was used as the carrier gas at a flow rate of 1.5 ml min^{-1}. Both total ion and selective-ion monitoring (SIM) modes were utilized. 2 μl of sample was injected into the GC–MS using splitless mode with an injection time of 2 min. The injection temperature was set at 250 °C, and the interface temperature at 280 °C. The GC temperature program was as follows: initial temperature 50 °C held for 2 min, then increased at 10 °C min^{-1} to 300 °C and held for 3 min. PCB and OCP standards, and samples were analysed separately in SIM mode with a detector voltage of 1.5 kV and a mass scan range between *m*/*z* 50 and *m*/*z* 500. The most abundant ion was selected as the quantitative ion, with a further two ions used for confirmation of each analyte [35].

3. Results and discussion

3.1. Method optimization and performance

The MASE conditions were optimized with respect to temperature and duration. The volume of water used for sample extraction in this work was not optimized, as the minimum amount of solvent volume recommended by the manufacturer of the microwave extraction system was only 8 ml. This was sufficient for complete immersion of the sediment sample in the extraction solvent. Based upon the above considerations, we chose to minimize the solvent volume for extraction, since a higher solvent volume considerably decreases analyte enrichment.

Many POPs are halogenated and are characterized by a low solubility in water and a high affinity to sediments [5]. A high external energy source is required to extract POPs from sediment. The effect of temperature (over the range of room temperature (25 °C) (without microwave digestion, direct-LPME of sediments) to 100 °C) on extraction efficiency is shown in Fig. 1a and b. An increase in extraction efficiency can be noted for most OCPs up to 80 °C. This can be attributed to the fact that an increased temperature decreases the partition coefficient between analytes and the sediment phase, thereby increasing the desorption rate of the POP from the solid to the aqueous phase However, above 80 °C a slight decrease in analyte enrichment (based on peak area measurements) was observed for some OCPs and PCBs. A temperature of 80 °C was selected for further optimisation of the method.

The time required for MASE is short compared to conventional Soxhlet extraction or conventional heating [15]. Digestion time was evaluated between 0 (direct LPME without microwave digestion) and 30 min (at 5-minute intervals), and a time of 20 min was found to be optimal. A longer digestion time did not result in any considerable increase in analyte yield for the majority of analytes (Fig. 2a and b). (LPME was carried out for 30 min.) Therefore, 20 min was selected as MASE time for further optimization of the method.

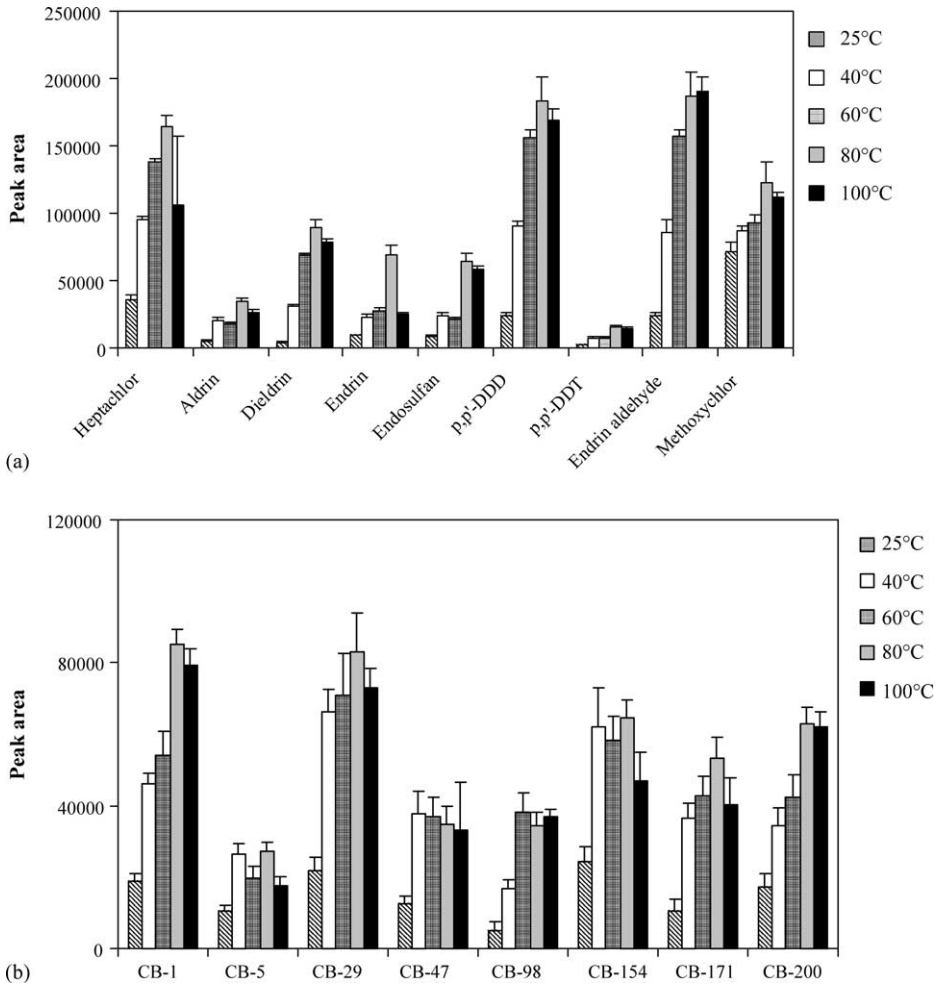

Fig. 1. Effect of MASE temperature on (a) OCP and (b) PCB extraction and compared with direct LPME at 25 °C.

LPME–HFM is an equilibrium process which involves the partitioning of analytes from an aqueous sample to a solvent phase within the porous HFM according to the partition coefficient of the analyte. The POPs studied are hydrophobic organic compounds, where the log values of octanol-water partition coefficients (K_{ow}) range from 2.8 to 8.2 and the water solubilities vary widely. For example, *p,p′*-DDT has a water solubility of 5 μg l^{-1} and BHC 7.3 mg l^{-1}.

It is well known that POPs have a higher affinity for sediment and tissue samples [9] than for the aqueous phase. For this reason, POPs were spiked at concentrations of between 10 (below the solubility limit in water) and 500 ng g^{-1} (above the solubility limit in water). At higher spiking concentrations, analytes are easily transferred to the aqueous phase, whereas at lower spiking concentrations external energy is required to release POPs from the sediment. After MASE, the analytes are in the aqueous phase and the analytes are then transferred into toluene prior to GC–MS analysis. Again, constant magnetic stirring facilitated the transfer of analytes from the aqueous phase to the organic solvent and reduced de-adsorption. Therefore, these analytes may be expected to partition readily into the organic solvent held within the HFM. The extraction efficiencies of OCP and PCB analytes under different microextraction times were tested between 5 and 30 min time. 20 min is sufficient for analytes to attain an equilibrium in the toluene solvent phase with a longer duration having no, or marginal, improvement in peak areas for most analytes.

The optimised MASE–LPME–HFM procedure proved to be both simple and effective for the POPs studied. OCP and PCB calibration was performed with five samples of uncontaminated sediment, each spiked with analyte concentrations ranging from 5 to 500 ng g^{-1}. The correlation coefficient (r) values ranged between 0.998, and 0.996 for OCP and PCB analytes respectively (see Table 1). The relative standard deviation (RSD) of each analyte was calculated based on triplicate analysis of sediment spiked at 50 ng g^{-1}, and the percentage RSD ranged from 4 to 20%. LODs were calculated by progressively decreasing the analyte concentration in the spiked sample such that GC–MS–SIM signals were clearly discerned at S/N of 3 at the final lowest concentration. LODs varied between 0.1 and 0.7 ng g^{-1} for OCPs and for PCBs between 0.1 and 0.6 ng g^{-1}.

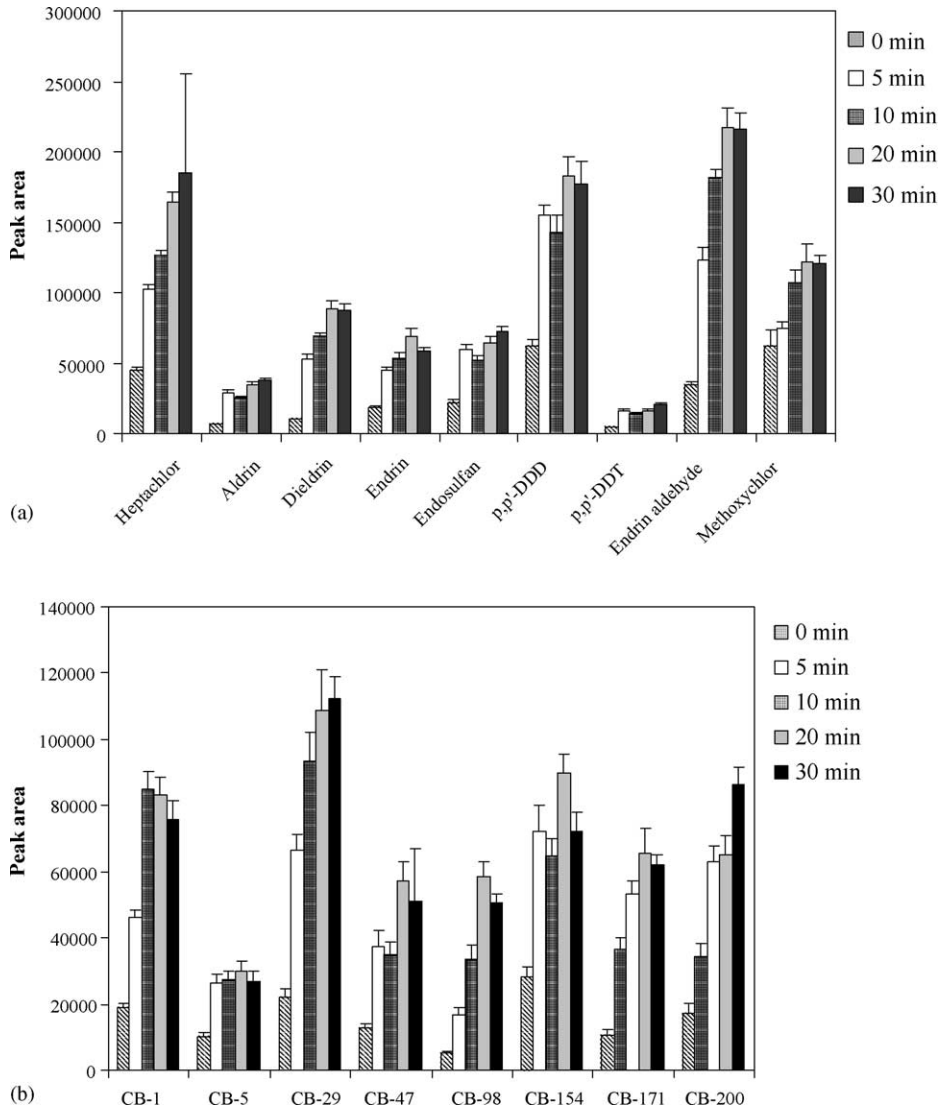

Fig. 2. Effect of MASE time on (a) OCP and (b) PCB extraction at 80 °C with direct LPME (0 min at 25 °C).

The percentage relative recovery for each analyte was determined for the MASE–LPME–HFM procedure by comparing the amount of analyte added to a field sediment sample with the concentration recovered from uncontaminated sediment samples. For field sediments spiked with 50 ng g^{-1} per analyte, extraction recoveries were calculated using standard addition recoveries and results are given in Table 2. Analyte recoveries exceeded 85% for all analytes

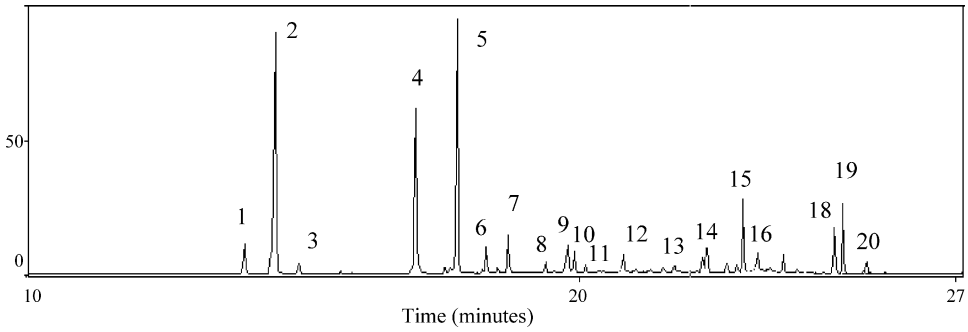

Fig. 3. Total ion chromatogram of PCBs and OCPs extracted from sediment samples spiked with 50 ng g^{-1} per analyte using MASE–LPME–HFM. Peak identification: (1) CB-1, (2) α-HCH, (3) CB-5, (4) Lindane, (5) β-HCH, (6) CB-29, (7) CB-47, (8) Heptachlor, (9) Aldrin, (10) CB-98, (11) CB-154, (12) Dieldrin, (13) Endrin, (14) Endosulfan II, (15) *p,p′*-DDD, (16) *p,p′*-DDT, (17) CB-171, (18) CB-200, (19) Endrin aldehyde and (20) Methoxychlor.

Table 1
Linearity range of calibration plots, limits of detection (LODs) and precision (%RSD) of MASE–LPME–HFM

Analyte	Correlation[a] coefficient	Equation	LODs (ng g^{-1})	RSD[b](%)
OCPs				
α-HCH	0.966	$y = 4220.7x - 630913$	0.1	17
Lindane	0.973	$y = 588.31x + 50603$	0.2	19
β-HCH	0.992	$y = 616.36x - 12458$	0.4	14
Heptachlor	0.998	$y = 2648.8x - 21704$	0.2	20
Aldrin	0.983	$y = 1750.6x - 209267$	0.2	19
Dieldrin	0.994	$y = 376.72x - 42550$	0.1	8
Endrin	0.998	$y = 605.14x - 21321$	0.1	19
Endosulfan	0.971	$y = 1091.6x - 168867$	0.2	8
p,p′-DDD	0.991	$y = 268.58x - 30759$	0.1	11
p,p′-DDT	0.992	$y = 931.92x - 11337$	0.1	14
Endrin aldehyde	0.983	$y = 972.49x - 148375$	0.7	17
Methoxychlor	0.998	$y = 49.185x - 2667.8$	0.1	12
PCBs				
CB-1	0.961	$y = 281.04x - 49051$	0.3	7
CB-5	0.996	$y = 3877.2x + 282853$	0.1	16
CB-29	0.993	$y = 1763.5x + 591381$	0.3	4
CB-47	0.984	$y = 1687x - 197539$	0.3	5
CB-98	0.993	$y = 298.94x + 42534$	0.4	16
CB-154	0.993	$y = 1016.6x - 113193$	0.5	4
CB-171	0.995	$y = 1005.4x - 26056$	0.6	11
CB-200	0.994	$y = 1136.8x - 136161$	0.6	16

[a] Linearity range 5–500 ng g^{-1}.
[b] $n = 3$.

with the exception of Lindane at 73%. Overall, the optimized novel method had comparable or better analyte extraction efficiencies than multi-step Soxhlet extraction for most analytes, with comparable RSD values.

Fig. 3 shows the chromatogram of OCPs and PCBs in sediment extracts when spiked at 50 ng g^{-1} to real sediment samples using the MASE–LPME–HFM procedure. A clean separation is readily achieved with the absence of sample

Table 2
Recoveries, RSDs of MASE–LPME–HFM and Soxhlet extraction and SPE

Analyte	Blank sediment (ng g^{-1})	MASE–LPME ($n = 3$)[a]		Soxhlet extraction ($n = 3$)[b]	
		Relative recovery (%)	RSD (%)	Recovery (%)	RSD (%)
OCPs					
α-HCH	6	108	7	89	10
Lindane	7	73	4	88	10
β-HCH	40	86	10	58	9
Heptachlor	5	96	9	65	19
Aldrin	8	117	11	104	16
Dieldrin	5	85	15	112	27
Endrin	7	99	2	107	21
Endosulfan	6	87	13	69	15
p,p′-DDD	Not detected	96	7	76	8
p,p′-DDT	3	108	6	67	15
Endrin aldehyde	1	90	16	97	4
Methoxychlor	3	111	9	57	12
PCBs					
CB-1	2	101	1	66	10
CB-5	1	108	7	59	11
CB-29	5	101	11	81	13
CB-47	1	86	12	92	13
CB-98	2	109	8	77	15
CB-154	2	89	14	96	13
CB-171	1	91	10	76	14
CB-2006	6	106	12	96	13

[a] POPs spiked at 50 ng g^{-1}.
[b] POPs spiked at 100 ng g^{-1}.

Table 3
OCP and PCB concentrations in marine sediment from northeastern and southwestern regions of Singapore's coastal environment

Analyte	Concentrations (ng g^{-1} dry wt.)			
	Northeastern region (n = 12)		Southwestern region (n = 12)	
	Mean	Min–Max	Mean	Min–Max
OCPs				
α-HCH	54	12–85	45	13–90
Lindane	14	4–25	18	4–45
β-HCH	128	108–156	126	43–179
Heptachlor	2	2–3	2	2–3
Aldrin	4	3–6	15	2–36
Dieldrin	78	60–103	94	73–107
Endrin	59	17–87	60	29–89
Endosulfan	12	4–27	32	6–50
p,p'-DDD	3	2–4	10	4–15
p,p'-DDT	5	2–9	6	1–15
Endrin aldehyde	17	12–26	14	2–34
Methoxychlor	3	2–5	57	57–57
PCBs				
CB-1	2	1–4	2	1–2
CB-5	3	1–4	2	1–3
CB-29	10	5–13	14	8–22
CB-47	5	0.2–11	5	5–5
CB-98	6	2–12	5	2–10
CB-154	4	3–6	1	n.d.–1
CB-171	4	2–7	2	2–2
CB-200	6	1–14	2	1–3

matrix interference. Overall, the MASE–LPME–HFM procedure is simple, rapid, and cost-effective where only few microlitres of solvent are required. Furthermore, the use of disposable HFM eliminates any analyte carry-over problem during sample analysis. The optimized MASE–LPME–HFM procedure was then used to determine the prevalence and concentrations of OCPs and PCBs in marine sediments sampled from Singapore coastal environment.

3.2. POPs in marine sediments

POPs have a lower solubility in seawater than in freshwater and are environmentally recalcitrant. They readily bind to surface plankton and other organic particulates and readily undergo sedimentation. The mean concentrations of individual POPs in sediments extracted from the northeastern and southwestern coastal areas of Singapore are shown in Table 3. The total mean OCP and PCB concentrations determined ranged from 325 to 678 ng g^{-1} and 10–61 ng g^{-1}, respectively. BHCs, Dieldrin and Endrin were more abundant in the all sampled locations. The low molecular weight PCB compounds i.e. monochloro and dichloro congeners were present at relatively low concentrations in comparison to the high molecular weight congeners, which predominated in the marine sediments. The probable reason is that the low molecular compounds are more readily volatilized to the atmosphere, whereas the higher molecular weight compounds can be expected to partition onto the particulate phase and undergo sedimentation.

4. Conclusions

The optimized MASE–LPME–HFM procedure has been successfully applied for the analysis of OCPs and PCBs in sediments collected from Singapore's marine coastal waters. The LODs, dynamic linear range and analytical precision of the method are impressive when compared with a conventional Soxhlet extraction and SPE cleanup procedure. Results obtained with analyte-spiked sediment prove that the method can be used for the rapid quantification of OCP and PCB compounds present at trace levels in marine sediments. The procedure is relatively simple, requires a low volume of solvent and eliminates carry-over effects through the use of disposable HFM.

Acknowledgements

The authors gratefully acknowledge the financial support of this research by the National University of Singapore and the United Nations University, Japan. This project was also supported by the Tropical Marine Science Institute, National University of Singapore.

References

[1] T. Colborn, M.J. Smolen, Rev. Environ. Contam. Toxicol. 146 (1996) 91.
[2] J.O. Allen, N.M. Dookeran, K.A. Smith, A.F. Sarofim, K. Taghizadeh, A.L. Lafleur, Environ. Sci. Technol. 30 (1996) 1023.
[3] R. Simò, J.O. Grimalt, J. Albagiés, Environ. Sci. Technol. 31 (1997) 2697.
[4] P. Fernàndez, R.M. Vilanova, C. Martinez, P. Appleby, J.O. Grimalt, Environ. Sci. Technol. 34 (2000) 1906.
[5] M.D. Erickson, Analytical Chemistry of PCBs, second ed., CRC Press, New York, 1997.
[6] J.S. Waid, PCBs and the Environment, CRC Press, Boca Raton, FL, USA, 1990.
[7] S. Liu, J.D. Ple, J. Chromatogr. B 796 (2000) 155.
[8] M. Cleemann, F. Riget, G.B. Paulsen, J. Klungsøyr, R. Dietz, Sci Tot. Environ. 245 (2000) 87.
[9] L. Asplund, B.G. Svensson, A. Nilsson, U. Eriksson, B. Jansson, S. Jensen, U. Wideqvist, S. Skerfving, Arch. Environ. Health 49 (1994) 477.
[10] S.P. Frost, J.R. Dean, K.P. Evans, K. Harradine, C. Cary, M.H.I. Comber, Analyst 122 (1997) 895.
[11] M.M. Schantz, J.J. Nichols, S.A. Wise, Anal. Chem. 69 (1997) 4210.
[12] K. Li, M. Landriault, M. Fingas, M. Liompoart, Analusis 26 (1998) 365.
[13] N. Saim, J.R. Dean, Md.P. Abdulla, Z. Zakaria, J. Chromatogr. A 791 (1997) 361.
[14] V. Lopez-Avila, R. Young, J. AOAC Int. 81 (1998) 1097.
[15] L. Jassie, R. Revesz, T. Kierstead, E. Hasty, S. Metz, in: H.M. Kingston, S.J. Haswell (Eds.), Microwave-Enhanced Chemistry,

American Chemical Society, Washington, DC, USA, 1997, p. 59.
[16] I.J. Barnabas, J.R. Dean, I.A. Fowlis, S.P. Owen, Analyst 120 (1995) 1897.
[17] A. Pastor, E. Vĭazquez, R. Ciscar, M. de la Guardia, Anal. Chim. Acta 344 (1997) 241.
[18] J.A. Dean, Lange's Handbook of Chemistry, 13th ed., McGraw-Hill, New York, 1985, pp. 10–28.
[19] G. Xiong, B. Tang, X. He, M. Zhao, Z. Zhang, Z. Zhang, Z. Zhang, Talanta 48 (1999) 333.
[20] C. Sparr Eskilsson, E. Björklund, J. Chromatogr. A 902 (2000) 227.
[21] G. Shen, H.K. Lee, J. Chromatogr. A 985 (2003) 167.
[22] J.J. Johnston, E.E. Petty, S.A. Volz, J. High Resol. Chromatogr. 20 (1997) 405.
[23] J.R.J. Pare, G. Matni, J.M.R. Belanger, K. Li, C. Rule, B. Thibert, V. Yaylayan, Z. Liu, D. Mathe, P. Jacquault, J. AOAC Int. 80 (1997) 928.
[24] S.J. Stout, A.R. da Cunha, G.L. Picard, M.M. Safarpour, J. Agric. Food. Chem. 44 (1996) 3548.
[25] R.A. Doong, P.L. Liao, J. Chromatogr. A 918 (2001) 177.
[26] Y.Z. Luo, J. Pawliszyn, Anal. Chem. 72 (2000) 1058.
[27] G. Shen, H.K. Lee, Anal. Chem. 74 (2002) 648.
[28] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (1999) 2650.
[29] K.E. Rasmussen, S. Pedersen-Bjergaard, M. Krogh, H.G. Ugland, T. Gronhaug, J. Chromatogr. A 873 (2000) 3.
[30] S. Pedersen-Bjergaard, K.E. Rasmussen, Electrophoresis 21 (2000) 579.
[31] L. Hou, H.K. Lee, J. Chromatogr A 1038 (2004) 37.
[32] S. Gang, H.K. Lee, Anal. Chem 75 (2003) 98.
[33] L. Sun, H.K. Lee, J. Chromatogr. A 1014 (2003) 165.
[34] C. Basheer, R. Balasubramanian, H.K. Lee, J. Chromatogr. A 1016 (2003) 11.
[35] C. Basheer, J.P. Obbard, H.K. Lee, Water. Air. Soil. Pollut. 149 (2003) 295.