Headspace solid phase microextraction in the determination of pesticides in water samples from the Okavango Delta with gas chromatography-electron capture detection and time-of-flight mass spectrometry

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ABSTRACT

Headspace solid phase microextraction (HS-SPME) was optimized for the analysis of pesticides with gas chromatography electron capture detection (GC-ECD) and high-resolution mass spectrometry. Factors influencing the extraction efficiency such as fiber type, extraction mode and temperature, effect of ionic strength, stirring and extraction time were evaluated. The lowest pesticide concentrations that could be detected in spiked aliquots after HS-SPME–GC-ECD ranged from 0.0005 to 0.0032 μg L^{-1}. Consequently hexachlorobenzene, trans-chlordane, 4,4′-DDD and 4,4′-DDE were detected in water samples after HS-SPME at concentrations ranging from 2.4 to 61.4 μg L^{-1} that are much higher than the 0.1 μg L^{-1} maximum limit of individual organochlorine pesticides in drinking water set by the European Community Directive. The same samples were cleaned with ISOLUTE C_{18} SPE sorbent with an optimal acetone/n-hexane (1:1 v/v) mixture for the elution of analytes. No pesticides were detected after SPE clean-up and pre-concentration. Precision for both methods was satisfactory with relative standard deviations less than 20%. This work demonstrated the superiority of HS-SPME as a sample clean-up and pre-concentration technique for pesticides in water samples as well as the need to identify and control point sources of pesticides.

1. Introduction

Water, a key constituent of ecosystems, is a recipient of a variety of xenobiotics such as pesticides and industrial chemicals by way of direct discharges from point sources or contaminated storm water run-off [1]. Organochlorine pesticides (OCPs), in particular, have a potential to give rise to serious ecological effects in freshwater environments due to their resistance to biological, chemical and photo-degradation [2]. Not only do OCPs have lethal toxic effects on aquatic organisms such as fish, but they bioaccumulate and biomagnify up in the food chain and exert carcinogenic and reproductive consequences in animals and human beings [3]. As a result, regulatory bodies such as the European Community have set the maximum concentrations of individual OCPs in drinking water at 0.1 μg L^{-1} and the total amount of pesticides at 0.5 μg L^{-1} [4]. Maximum individual concentrations for aldrin, dieldrin and heptachlor epoxide have even been set lower at 0.03 μg L^{-1} [5]. There is therefore, a need for highly sensitive analytical methods involving sample preparation techniques with high pre-concentration capacities for monitoring environmental pollutants especially in water employed for human consumption to keep these levels in check.

Sample preparation is often considered to be a fundamental step in the analytical procedure because it not only helps to achieve the low detection limits set by regulatory authorities by cleaning up the sample matrix but also pre-concentrates analytes of interest from a dilute sample matrix for positive identification [6]. Traditional sample preparation methods for water samples such as liquid–liquid extraction (LLE) and solid phase extraction (SPE) were laborious and consumed considerable amounts of organic solvents [7,8] however, modern microextraction techniques such as solid phase microextraction (SPME), stir-bar sorptive extraction (SBSE), liquid-phase microextraction (LPME) require minimal handling and consumption of organic solvents as well as offer high selectivity and enrichment factors [9].

SPME, introduced by Pawliszyn in 1989, is a well established solvent-free, easy to use, rapid and portable sample preparation method that is compatible with several analytical instruments such as GC and HPLC [10,11]. It is based on the partitioning of analytes between the sample matrix and the polymeric fiber coating and their subsequent desorption on the injection port of a chromatograph [12]. The major advantage of SPME is that it incorporates sample extraction, clean-up and pre-concentration of a wide variety of compounds from both solid and liquid matrices into a single procedure [13,14]. Since its development, SPME has been applied to the analysis of environmental, food, biological and pharmaceutical samples [15,16].

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The study aims at employing the high enrichment capacity of SPME for screening pesticides in water samples from the Okavango Delta, Botswana. Described in this paper is the optimization procedure for SPME, its application to water samples and a performance comparison to SPE. Gas chromatography with electron capture detection (GC-ECD) was employed followed by confirmation with high-resolution gas chromatography–time of flight-mass spectrometry (GC–ToF-MS).

2. Experimental

2.1. Standards, reagents and materials

α-Benzenehexachloride (α-BHC) (97.9%), β-benzenehexachloride (β-BHC) (98.0%), γ-benzenehexachloride (γ-BHC) (99.8%), heptachlor (98.5%) and methoxychlor (98%) were obtained from Supelco (Bellafonte, PA, USA). Aldrin (98.1%), trans-chlordane (98.4%), 2, 4′-DDD (99.7%), 4, 4′-DDD (98.9%), 4, 4′-DDE (99.5%), 4, 4′-DDT (99.6%), dichlorvos (99.7%), dieldrin (97.9%), endrin (99.1%), β-endosulfan (99.9%) and hexachlorobenzene (HCB) (99.6%) were obtained from Riedel-de-Haën (Seelze, Germany). Stock solutions of each pesticide were prepared in acetone at 100 mg L^{-1} concentrations (except for dichlorvos whose stock solution was 1000 mg L^{-1}) as well as intermediate standard solutions at 10 and 1 mg L^{-1} concentrations. For SPME work, a 1–10 mg L^{-1} working standard mixture was prepared containing 1 mg L^{-1} each of aldrin, α–BHC, γ-BHC, HCB and heptachlor, 2 mg L^{-1} each of 4,4′-DDE and dieldrin, 3 mg L^{-1} each of β-BHC, 4,4′-DDT and β-endosulfan, 4 mg L^{-1} each of 2,4′-DDD, 4,4′-DDD and endrin, 5 mg L^{-1} of chlordane as well as 10 mg L^{-1} of methoxychlor. The working standard mixture employed for SPE studies was similar to that employed for SPME work except that dichlorvos (50 mg L^{-1}) was used in place of methoxychlor due to lack of availability of methoxychlor.

Sodium chloride was obtained from Merck (Milan, Italy). HPLC/UV grade acetone, dichloromethane and n-hexane were obtained from Ultrafine Limited (London, England). Ultra high purity (UHP) water was generated from a Millipore Alpha-Q system supplied by Millipore (Molsheim, France). Silica SPME fibers (7 μm PDMS, 30 μm PDMS, 100 μm PDMS, 65 μm PDMS/DVB and 85 μm PA) and amber glass screw cap vials (4 ml) for SPME with polytetra fluoroethylene (PTFE)/silicone septa (75 mm thick) were obtained from Supelco (Bellafonte, PA, USA). ISOLUTE C_{18} cartridges were obtained from International Sorbent Technology Ltd (Mid Glarmogan, UK).

2.2. Instrumentation

During sampling, the water conductivity, dissolved oxygen and pH were measured using Cond 330i/SET, Oxi 330i/SET and pH 340i/SET respectively, all manufactured by Wissenschaftlich-Technische Werkstätten (Weilheim, Germany).

Routine analysis was performed on an Autosystem XL gas chromatograph manufactured by Perkin Elmer (Norwalk, CT, USA) equipped with a split–splitless injector and a ^{63}Ni electron-capture detector (ECD). A Zebron ZB-35 (35% phenyl and 65% dimethylsiloxane) fused silica capillary column 30 m×0.25 mm×0.25 μm (film thickness) manufactured by Phenomenex (Torrence, CA, USA) was employed in the separation of analytes.

Analytes were confirmed on a 6890 N gas chromatograph equipped with a 7683B autosampler manufactured by Agilent Technologies (Shangai, China) connected to a GCT Premier Time-of-flight mass spectrometer manufactured by Waters (Manchester, England).

2.3. The study area

The Okavango Delta, situated in the north west of Botswana, is the world's largest Ramsar wetland site covering an area of 16 000 km^2 and a habitat for a wide variety of wildlife, birds and fish [17]. As is the case for most typical wetlands, the Okavango Delta is characterized by high concentrations of dissolved organic matter (DOM) — mostly humic and fulvic substances that give the water its brownish tea colour and functions by supporting growth of heterotrophic microorganisms [18]. Independent studies by McCarthy et al. [19] and Huntsman-Mapila and colleagues [20] reported that Ca^{2+} and Mg^{2+} were the major cations while HCO_3^- was the major anion in water from the delta. Due to the prevalence of malaria, indoor spraying with dichlorodiphenyltrichloroethane (DDT) has been reported in the area as far back as the mid-1940s and was discontinued in 1998 when the public health authorities switched to pyrethroids [21].

2.4. Sample collection

Water samples (100 ml) were collected in glass bottles between September 2005 and September 2006 from Chief's Island, Guma Lagoon, Lake Ngami, Maun, Mohembo, Samochima, Sepopa Water Swamp, Shakawe, Toteng and Xakanaxa in the delta (all sites are shown in Fig. 1).

The water conductivity, dissolved oxygen and pH were measured at each sampling point. Samples were acidified with 1 ml of nitric acid (1 M) and the bottles sealed immediately after sampling and stored in ice while in the field. Upon arrival at the laboratory the samples were filtered through 0.45 μm filter membranes to remove particulate matter and preserved in a cold room at 4 °C prior to analysis.

2.5. Chromatographic conditions

2.5.1. GC-ECD

The Perkin Elmer Autosystem XL GC was operated in the splitless mode with ultra high purity (99.999%) nitrogen employed as carrier gas at a column head pressure of 14 psi. The injector and detector temperatures were set to 250 and 300 °C, respectively. The oven temperature was programmed from an initial value of 50 °C (hold 1 min), ramped to 200 °C at a rate of 40 °C/min (hold 2 min), ramped to 240 °C at a rate of 4 °C/min (hold 1 min) and finally ramped to 270 °C at a rate of 4 °C/min (hold 5 min). The injection volume was 1 μl at all times.

2.5.2. GC–ToF-MS

The column and oven temperature program employed in Section 2.5.1 were used in the GC-MS system. Helium was employed as a carrier gas at a rate of 1 ml/min. The injector and transfer line temperatures were both maintained at 250 °C while the ion source was kept at 220 °C. The electron impact (EI) source was operated at 70 eV and the mass spectra were acquired from 50 to 500 *m/z* with a detector voltage of −2700 V. The acquisition rate was 10 spectra s^{-1}. The solvent delay time was set to 3.8 min. Mass spectra were compared to the NIST/EPA/NIH Mass Spectral Library-2005 Version (Newfield NY, USA).

2.6. SPME optimization

Before use, the fibers were conditioned for 2 h in the injection port of the GC-ECD according to the manufacturer's instructions while maintaining the GC oven and detector at 200 and 300 °C, respectively. A blank injection was performed to confirm removal of impurities from the GC system. Other blank experiments also carried out were those of fiber blanks, a blank of the fiber inserted into an empty vial, a vial containing 0.5 g NaCl and a vial containing 2 ml of ultra pure water. For all the optimization experiments, a 2 ml aliquot of ultra high purity water (adjusted to pH 6.5) was placed into a 4 ml vial and spiked with 20 μl of 1–10 mg L^{-1} pesticides standards mixture. Initially the extractions were carried out at 60 °C and the extraction time set to 30 min. Thermal desorption on the GC injection port was carried out at 250 °C for 5 min.

The extraction efficiencies of the available fibers were evaluated by direct immersion of the fibers into spiked water aliquots. 65 μm PDMS/

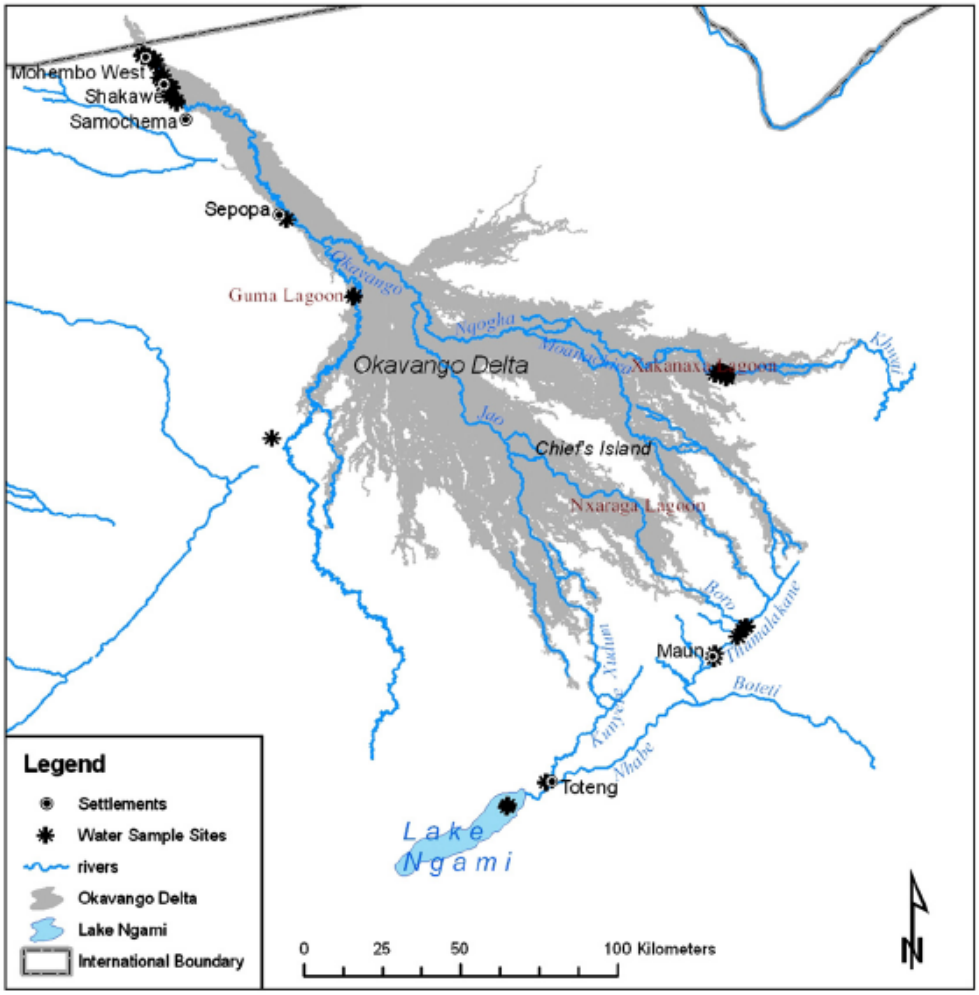

Fig. 1. Map of the Okavango Delta showing sampling areas.

DVB fiber gave the highest peak areas and hence it was chosen for the subsequent experiments. Both direct immersion (DI) and headspace (HS) extraction modes were evaluated employing 65 μm PDMS/DVB fiber and the peak areas compared. The effect of temperature on the extraction efficiency was investigated at temperatures 40, 60 and 80 °C. Highest extraction efficiencies were obtained at 80 °C. The effect of ionic strength on the extraction efficiency was investigated by adding 10, 20, 30, 40 and 50% of NaCl (w/v) to the spiked water. The vials were covered and swirled for 1 min to dissolve the salt before extraction. Addition of 10% NaCl gave the highest extraction efficiencies. The effect of agitation on the extraction efficiency was studied at a maximum speed of 300 rpm. A precaution was taken to modify the stirring bar by covering it with glass to prevent adsorption of pesticides onto the stirrer coating [22]. No positive effect was observed hence no stirring was employed for subsequent experiments. The extraction profiles of pesticides at 80 °C were constructed for different times (15, 30, 45 and 60 min). The optimal time was 30 min.

2.7. SPE optimisation

The pH of a 30 ml aliquot of ultra high purity water was adjusted to 6.5. The aliquot was spiked with 100 μl of the 1–50 mg L^{-1} standard mixture. The ISOLUTE C_{18} sorbent was conditioned with 2 ml methanol (MeOH) and equilibrated with 2 ml ultra high purity water. The spiked 30 ml aliquot was eluted at a rate of 2 ml/min and the SPE sorbent was dried under vacuum for 30 min. Six elution solvents were investigated namely CH_2Cl_2 (100%), CH_2Cl_2/acetone (1:1 v/v), CH_2Cl_2/MeOH (9:1), CH_2Cl_2/MeOH (1:1 v/v), acetone/n-hexane (1:1 v/v) and $CHCl_3$/n-hexane (1:1 v/v). The eluate was evaporated to complete dryness under a stream of N_2 gas. The analytes were reconstituted in 100 μl acetone/n-hexane (1:1 v/v). 1 μl was then analysed by GC-ECD and peak areas of each pesticide were compared to those in an equal volume of standard mixture which had been similarly dried and reconstituted. The elution solvent system that gave the highest recoveries for most pesticides was acetone/n-hexane (1:1 v/v) and hence was chosen for the analysis of water samples.

2.8. Analytical parameters

The linearity of the SPME method was studied by employing aliquots of ultra pure water spiked at concentrations between (0.0001–0.0010) and (0.0100–0.1000) μg L^{-1} of the standard mixture. Similarly, the linearity of the SPE method was studied using spiked aliquots at concentrations ranging from (10–500) to (1000–50 000) μg L^{-1}.

Calibration concentrations ranged between (0.001–0.010) and (100–5 000) μg L^{-1} for SPME and SPE, respectively. The SPME and SPE method determination limits (SPME and SPE-LDs) were defined as the lowest pesticides concentrations that could be determined from a spiked aliquot of ultra pure water employing SPME or SPE sample preparation procedures based on the GC-ECD signal-to-noise (S/N) ratio of 3:1 for individual peaks.

2.9. Application of optimized HS-SPME and SPE to water samples

The optimized HS-SPME and SPE conditions were applied to the sixty-one water samples (pH adjusted to 6.5) and analysed by GC-ECD while GC-ToF-MS was used for confirmation of analytes.

3. Results and discussion

3.1. SPME optimization

Results displayed in Fig. 2 show that 65 μm PDMS/DVB fiber gave the highest peak areas followed by 30 μm PDMS and 85 μm PA fibers while 7 μm PDMS performed poorly for most pesticides. Some pesticides such as HCB, α-BHC, β-BHC, γ-BHC, 4,4′-DDE, endrin and 4,4′-DDD were extracted onto the 85 μm PA fiber (that is the most suitable for polar compounds) with efficiencies similar to the 65 μm PDMS/DVB fiber. Methoxychlor was the only pesticide that was extracted onto 7 μm PDMS with the highest efficiency. As expected for semi-volatile and volatile compounds, HS-SPME was more sensitive than the DI mode since HS sampling eliminates competition for adsorption sites on the fiber coating by non-volatile compounds present in the liquid sample [23].

The addition of 10% (w/v) NaCl introduced a slight improvement in the extraction efficiency of a majority of pesticides except for β-endosulfan and methoxychlor whereby the addition of 10% salt more than doubled the extraction efficiency of the fiber. Low recoveries for β-endosulfan have also been reported for HS-SPME by Lambropoulou and colleagues [24]. Increasing the salt content beyond 30% (w/v) showed a decline of the extraction efficiency for all the pesticides.

3.2. SPE optimisation

Dichlorvos was the least recovered pesticide at 52.6% recovery while 2, 4′-DDD had the highest recovery of 117.8% using the acetone/n-hexane (1:1 v/v) elution solvent. The low recovery of dichlorvos may be due to its polar character hence weak retention on the non-polar C_{18} sorbent as compared to the other pesticides. The acetone/n-hexane (1:1 v/v) solvent system gave the highest recoveries hence it was chosen for further clean up of samples.

Table 1
Analytical parameters obtained after SPME and SPE sample preparation techniques and subsequent analysis of pesticides by GC-ECD

Parameter	SPE	SPME
Linearity (μg L^{-1})	10–50 000	0.0005–0.1000
R^2	0.9980–0.9994	0.9989–0.9998
LDs (μg L^{-1})	31.0–510.0	0.0005–0.0030
% RSDs	5.3–15.0	5.2–14.0

3.3. Analytical parameters

Analytical parameters were obtained for SPME and SPE sample preparation methods by the analysis of different spiked ultra pure water samples employing pesticides standard mixtures described in Section 2.8. Linear relationships were obtained between peak areas and the analyte concentrations, with high correlation coefficients (≥0.9998). Table 1 shows that the limits of detection after SPE ranged from 31.0 to 510.0 μg L^{-1} (for aldrin and α-BHC, respectively). In HS-SPME the 65 μm PDMS/DVB fiber was most sensitive to trans-chlordane as it had the lowest SPME-LD of 0.00051 μg L^{-1}. Precision was determined by reproducibility studies expressed by percent relative standard deviation (% RSD) of 3 spiked water aliquots and was less than 15% for both methods. High % RSD values were obtained for compounds that were least recovered in each extraction technique (15.0% for dichlorvos after SPE and 14.0% for β-BHC after HS-SPME) and these could have been caused by poor selectivities of the SPE sorbent and SPME fiber to the analytes in the presence of matrix components González and co-workers [26] recommended employing a matrix-matched calibration rather than the solvent-based calibration so as to reduce variability of pesticides caused by matrix effects. Pankow [27] reported that injecting samples containing traces of water into the GC-ECD could lead to variations in the responses of the analytes. Traces of moisture could have been from the headspace of the water samples during SPME or inadequate drying of the SPE eluates. The variability of the water samples in terms of sampling locations, where sediment composition and vegetation type differ drastically, may have also impacted on the high % RSDs.

3.4. Water analysis

3.4.1. Application of optimized SPME method to the water samples

The optimized SPME method was employed to determine pesticides in water samples and four pesticides namely HCB, trans-chlordane, 4,4′-DDE and 4,4′-DDD were detected by GC-ECD at concentrations ranging between 2.4 and 61.4 μg L^{-1} as shown in Table 2.

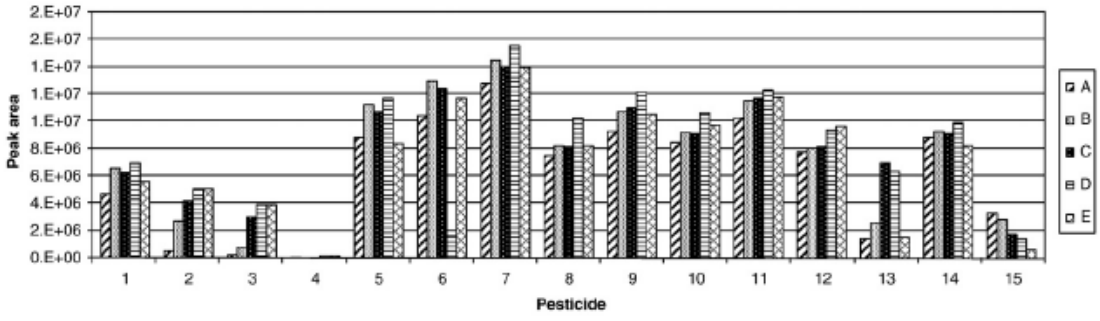

Fig. 2. Comparison of extraction efficiencies of five SPME fibers: A=7 μm PDMS; B=30 μm PDMS; C=100 μm PDMS; D=65 μm PDMS/DVB and E=85 μm PA. Pesticides are as follows: 1=HCB; 2=α-BHC; 3=γ-BHC; 4=β-BHC; 5=Heptachlor; 6=Aldrin; 7=trans-Chlordane; 8=4,4′-DDE; 9=Dieldrin; 10=2,4′-DDD; 11=Endrin; 12=4,4′-DDD; 13=β-Endosulfan; 14=4,4′-DDT; 15=Methoxychlor.

Table 2
Compounds detected in water samples after HS-SPME with GC-ECD and GC-ToF-MS

Pesticide	Concentration (μg L^{-1})	% RSD
HCB	61.4	7.9
Trans-chlordane	3.2	5.7
4,4′-DDE	5.3	9.4
4,4′-DDD	2.4	7.2
Isobutyl-4-octylester–phthalic acid	N.Q.	N.Q.
Dibutyl phthalate	N.Q.	N.Q.
DEHP	N.Q.	N.Q.

N.Q. — not quantified.

Phthalates (employed in the plastic industry) were also identified in the water samples but could not be quantified due to lack of pure standards. A chromatograph of a water sample after HS-SPME followed by GC-ECD is shown in Fig. 3.

3.4.2. Application of optimized SPE method to the water samples

The optimized SPE conditions were applied to the clean-up of water samples. The general profile of water samples collected along the main channel of the delta – also known as the 'Panhandle' (Mohembo, Shakawe, Samochema, Sepopa and Guma Lagoon) – differed from that of samples collected downstream (Maun, Toteng and Lake Ngami) next to lodges and villages. Compounds identified upstream were absent downstream probably due to degradation or change in pH from near-neutral upstream to alkaline downstream. Table 3 shows compounds detected in samples from the Panhandle and those from downstream after SPE clean-up.

Dodecamethylcyclosiloxane is employed in a variety of industrial products including household and car care products as well as chemical formulations [25]. DEHP is one of the main phthalates used as a plasticiser in the production of PVC and has been classified by the Environmental Protection Agency (EPA) as a possible human carcinogen substance [28].

Water samples collected downstream next to lodges and villages showed the presence of hydrocarbons such as dodecane ($C_{12}H_{26}$) hexadecane ($C_{16}H_{34}$), octadecane ($C_{18}H_{38}$), eicosane ($C_{20}H_{42}$), and 1,1,3,3-tetramethyl-1,3-dioctadecyldisiloxane. Hydrocarbons are naturally found in unpolluted environments as a result of biotransformation of plant materials but may also occur due to contamination from petroleum spills of combustion processes [29]. Low molecular weight hydrocarbons (n-C_{14}–n-C_{19}) are indicative of degradation of plant matter while high molecular hydrocarbons (>n-C_{20}) suggest possible petroleum contamination [30]. Even though hydrocarbon standards were not available for quantification, the presence of eicosane – a high molecular weight hydrocarbon – in water samples collected next to lodges and villages shows possible petroleum contamination of the delta's water due to point source pollution.

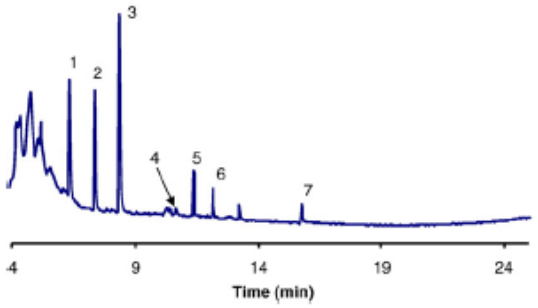

Fig. 3. A chromatogram of a water sample showing (1) HCB; (2) isobutyl-4-octylester phthalic acid; (3) dibutyl phthalate; (4) trans-chlordane; (5) 4,4′-DDE; (6) 4,4′-DDD and (7) diethylhexylphthalate after HS-SPME at 80 °C and 10% NaCl. The fiber employed was PDMS/DVB.

Table 3
Compounds detected in water samples after SPE with GC-ECD and GC–ToF-MS

Compound	Region in delta	Possible source
Dodecamethylcyclohexasiloxane	Upstream	Chemical formulations
Diethylhexylphthalate	Upstream	PVC products
α-hexylcinnamaldehyde	Upstream	Vegetation and wooden boats
Hydrocarbons (dodecane, hexadecane, octadecane and eicosane)	Downstream	Plant materials and petroleum spills
1,1-3,3-tetramethyl-1,3-dioctadecyldisiloxane	Downstream	PVC products

4. Conclusions

Pesticides were determined in water employing optimized HS-SPME with GC-ECD and confirmed by GC-ToF-MS. Satisfactory precision was obtained for both HS-SPME and SPE methods however HS-SPME exhibited a higher selectivity and sensitivity to pesticides with determination limits 3-fold lower than those for SPE. While no pesticides were detected after clean-up by SPE, HCB, trans-chlordane, 4,4′-DDE and 4,4′-DDD were detected with the HS-SPME method. Hence HS-SPME is recommended for environmental monitoring due to its high selectivity and high pre-concentration capacity. The authors recommend that analyses of phthalates and pesticides should be included in regular monitoring programs of the Okavango Delta ecosystem. Sources of contamination need to be identified and controlled to prevent further contamination of the Okavango Delta as well as reduce the present levels of pesticides in the water that are much higher than the recommended EU levels for drinking water.

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