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# Quantitative solid phase microextraction – Gas chromatography mass spectrometry analysis of the pesticides lindane, heptachlor and two heptachlor transformation products in groundwater

Sarah-Louise McManus[a,b], Catherine E. Coxon[b], Karl G. Richards[a,*], Martin Danaher[c]

[a] Teagasc, Johnstown Castle, Environmental Research Centre, Co Wexford, Ireland
[b] Department of Geology, Trinity College Dublin, Dublin 2, Ireland
[c] Food Safety Department, Teagasc Food Research Ashtown, Dublin 15, Ireland

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ABSTRACT

This paper describes the development and validation of a method for the determination of lindane, heptachlor and two heptachlor transformation products (*exo*- and *endo*-heptachlor epoxide) in groundwater. Samples were extracted using a simple solid phase microextraction (SPME) method with a polyacrylate fibre prior to detection by gas chromatography mass spectrometry in electron impact ionisation mode (GC–EI-MS). The linearity of the method ranged from 0.015 to 5.0 $\mu g\,L^{-1}$, with correlation coefficients greater than 0.99. Recoveries ranged from 96 to 101% at several fortification levels with all coefficients of variation (CV%) less than 10.5%. The method was validated to the permitted limits laid down in the European Union drinking water directive (98/83/EC). The limit of quantitation (LOQ) was 0.015 $\mu g\,L^{-1}$ in groundwater samples. Samples had to be analysed within 24 h of collection otherwise degradation occurred and disposable SPME polyacrylate fibres lasted up to 51 injections. Both *endo*-heptachlor epoxide and lindane were detected in groundwater samples with concentrations ranging between 0.033 and 0.048 $\mu g\,L^{-1}$.



## 1. Introduction

Groundwater serves as an important source of potable drinking water in the European Union (EU) [1]. In Ireland, between 26 and 75% of public and private drinking water supplies come from groundwater [2]. Groundwater also contributes to surface water flows, particularly in summer low flow periods. Hydrologically groundwater is connected to other water bodies and its contamination can impact on the environment, leading to deterioration in the quality of potable drinking water supplies. In 2000, the European Union (EU) introduced the Water Framework Directive (2000/60/EC) [3] for all EU member states. The objective of this directive was to protect and improve water quality, with a target to achieve 'good status' for all water bodies by 2015.

Lindane (γ-hexachlorocyclohexane, γ-HCH) was used as a broad spectrum insecticide to control phytophagous and soil inhabiting insects since the 1940s [4]. Lindane is produced from technical grade HCH, which contains eight different isomers [5]. HCH is also marketed as an insecticide but since γ-HCH is the only isomer that exhibits strong insecticidal properties, it has been common to refine and market it under the name "lindane" [5]. Lindane, α-HCH and β-HCH were categorised as persistent organic pollutants (POPs) under the Stockholm convention in 2009 [6]. The physico-chemical properties of lindane have been discussed by Xiao et al. [7]. HCH's are relatively volatile which has led to their global transport, even in locations such as the Arctic [5]. HCH's are one of the most widely detected organochlorine compounds in environmental samples including air, surface water, soil, and living organisms. Bhatt et al. [8] reported that HCHs can potentially impact on human health, due to impact on central nervous, endocrine, immune, and reproductive systems. It has also been reported that HCHs are probable carcinogens [6]. The drinking water directive (Council Directive 98/83/EC) [9] states that individual active ingredients (a.i.) present in water must not exceed the limit (previously referred to as the maximum allowable concentration (MAC) in older legislation [10]) of 0.1 $\mu g\,L^{-1}$ for individual compounds or 0.5 $\mu g\,L^{-1}$ for total a.i. found in any one sample.

Heptachlor has been used since the 1950s as an insecticide to kill termites and other soil insects [11]. It is reported that heptachlor can persist in soil for as long as 14 years [12]. The main transformation product is heptachlor epoxide, which exists in two isomeric forms: *exo*-heptachlor epoxide (isomer B) and *endo*-heptachlor

* Corresponding author. Tel.: +353 0539171200; fax: +353 0539142213.
*E-mail address:* karl.richards@teagasc.ie (K.G. Richards).

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epoxide (isomer A) with isomer B the more stable form in the environment [13]. As a result, heptachlor was listed on the original Stockholm Conventions "Dirty Dozen" POPs. The physico-chemical properties of heptachlor and heptachlor epoxide are reported by Shen and Wania [14]. The International Agency for Research and Cancer (IARC) has classified heptachlor as a possible human carcinogen [15] and residues are still encountered in the environment because of their high persistence and lipophilic properties [16], especially to sediments and terrestrial and aquatic organisms [13]. Heptachlor epoxide has been reported to be of greater toxicological significance because it is more stable and persists longer in the environment [17]. Therefore, it is important to monitor for both heptachlor and its epoxide transformation products in water. Council Directive 98/83/EC [9] has set a lower limit for heptachlor and heptachlor epoxide in drinking water of 0.03 $\mu g\,L^{-1}$.

There have been a number reports in the literature on the incidence of lindane and heptachlor residues in water samples. Willett et al. [18] carried out an extensive review of lindane and other HCH compounds in the environment. HCH residues in surface waters were reported to be higher in the Northern Hemisphere than in the Southern Hemisphere with HCH concentrations ranging from 0.0008 to 0.0036 $\mu g\,L^{-1}$ in water samples. Bhatt et al. [8] more recently reported HCH levels of 20.7–86.2 $\mu g\,L^{-1}$ in the drinking water supply for El Haram, Giza, Egypt. Surface waters in India studied by Singh et al. [19] reported lindane concentrations, in the form of α-HCH, up to 1.02 $\mu g\,L^{-1}$, heptachlor up to 0.06 $\mu g\,L^{-1}$, and heptachlor epoxide up to 0.06 $\mu g\,L^{-1}$. Groundwater in industrial areas of Berlin reported concentrations of 65 $\mu g\,L^{-1}$ for α-HCH [20]. The physico-chemical properties of lindane have been discussed by Walker et al. [5] and Willett et al. [18].

Several methods have been developed to test for organochlorine pesticides in river water [21] and seawater [22]. Faraji and Helalizadeh [21] developed a method to include the analysis of heptachlor and heptachlor epoxide in river water. The method detection limit for heptachlor and heptachlor epoxide were 0.05 and 0.04 $\mu g\,L^{-1}$, respectively. These detection limits are above the drinking water limit of 0.03 $\mu g\,L^{-1}$ in drinking water as specified in directive 98/83/EC [9]. Basheer et al. (2002) [22] developed a method for seawater to include lindane and heptachlor but not heptachlor's transformation products *exo*- and *endo*-heptachlor epoxide. Samples were extracted using liquid-phase microextraction (LPME) prior to detection by GC–MS. Limits of detection were 0.013 and 0.03 $\mu g\,L^{-1}$ for lindane and heptachlor, respectively. Other studies have developed methods for these four analytes because of concern about their bioaccumulation potential and persistence [21–23]. Chusaksri et al. [16] used SPE and liquid chromatography tandem mass spectrometry in APCI (atmospheric pressure chemical ionisation) mode to quantify for heptachlor and one transformation product of heptachlor; heptachlor epoxide (isomer not specified), with a linear range for heptachlor of 0.009–2.21 $\mu g\,L^{-1}$ while heptachlor epoxide had the range 0.24–11.52 $\mu g\,L^{-1}$ in surface water. Okumura et al. [24] determined heptachlor epoxide in pure water using GC–MS with a detection limit of 0.031 $\mu g\,L^{-1}$. Ratola et al. [25] used SPME and GC–ECD (Electron Capture Detection) to quantify for lindane and heptachlor to achieve detection limits of 0.097 and 0.05 $\mu g\,L^{-1}$, respectively in aqueous media. Again this detection limit for heptachlor is higher than the EU drinking water limit [9]. However, no method until now has yet determined both transformation products together with heptachlor and lindane.

In this work, analytes were isolated from water samples using solid phase microextraction (SPME). This technique was originally developed by Belardi and Pawliszyn [26] and has been widely applied by other groups for analysing pesticides and other micropollutants in surface water [27] and groundwater [28]. This technique is advantageous compared to liquid–liquid extraction and solid phase extraction (SPE) because it combines several sample preparation steps to reduce solvent usage, processing time and thus improving sample throughput. Until now no other method has determined both transformation products of heptachlor during the same chromatographic run or taken into consideration the levels permitted in ground- and drinking-water when undertaking validation.

## 2. Materials and methods

### 2.1. Reagents and materials

HPLC grade methanol was purchased from Reagecon (Shannon, Ireland) and deionized water with a conductivity of 0.055 $\mu S\,cm^{-1}$ was generated on site using a Sartorius Arium® 611 μV water purification system (Sartorius Stedim UK Ltd, Dublin, Ireland). SPME fibres were all purchased from Supelco™ (Sigma Aldrich, Arklow, Ireland) to include the coatings DVB/CAR/PDMS 23GA, 50/30 μm; PDMS-DVB 23GA; Polyacrylate 23GA, 85 μm and Carboxen/PDMS 23GA, 85 μm. HPLC p.a. puriss sodium chloride (NaCl) was purchased from Sigma Aldrich (Arklow, Ireland). 10 mL headspace vials with screw caps and PTFE septum 1.5 mm were purchased from InfoChroma (New Haven, USA).

### 2.2. Standards and calibration

Lindane, heptachlor, *exo*-heptachlor epoxide, and *endo*-heptachlor epoxide standard solutions (100 $\mu g\,mL^{-1}$ in methanol) were purchased from AccuStandard (NewHaven, CT, USA). The deuterated internal standard α-HCH-$D_6$ (100 $ng\,\mu L^{-1}$ in cyclohexane) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). A primary stock standard solution was prepared at a concentration of 100 $\mu g\,L^{-1}$ in methanol to contain all four compounds of interest. From this primary stock, intermediate working standards for a six point calibration were prepared in deionized water so as to contain less than 1% (v/v) solvent to target the concentrations: 0.015, 0.1, 0.5, 1.0, 2.0, and 5.0 $\mu g\,L^{-1}$. For validation studies intermediate working solutions were made to target the concentrations: 0.015, 0.03, 0.05, 0.1, and 0.15 $\mu g\,L^{-1}$. A working internal standard solution of 25 $\mu g\,L^{-1}$ was prepared and used to spike all samples for validation and application work to achieve 0.1 $\mu g\,L^{-1}$ of internal standard in each sample.

### 2.3. Sample preparation

Groundwater samples were analysed within five days of receipt to the laboratory. Five mL of sample was transferred into a 10 mL headspace vial containing 2.5 g NaCl to achieve 50% (w/v) saturation. The addition of salt improves extraction efficiency by reducing the solubility of analytes in the sample where by increasing the ionic strength of the sample [26,29]. Five mL of $H_2O$ was used because when the fibre was immersed in the sample this volume did not allow any sample to touch the barrel of the SPME fibre syringe which may allow for carry over and cross contamination. The penetration depth of the fibre was set to 28 mm.

### 2.4. SPME extraction

Extraction was carried out using a CTC Combi-pal auto-sampler (CTC Analytics AG, Switzerland) configured for SPME extraction using a Combi PAL SPME kit (CTC Analytics, Switzerland). Disposable SPME polyacrylate (PA) fibres were directly immersed in the sample vial and extracted at 50 °C for 45 min with agitation at 250 rpm. Agitation was used to accelerate the extraction, reducing time spent extracting [26]. Desorption of the fibre took place in a Varian 1079 injector at 250 °C in splitless mode for 4 min following

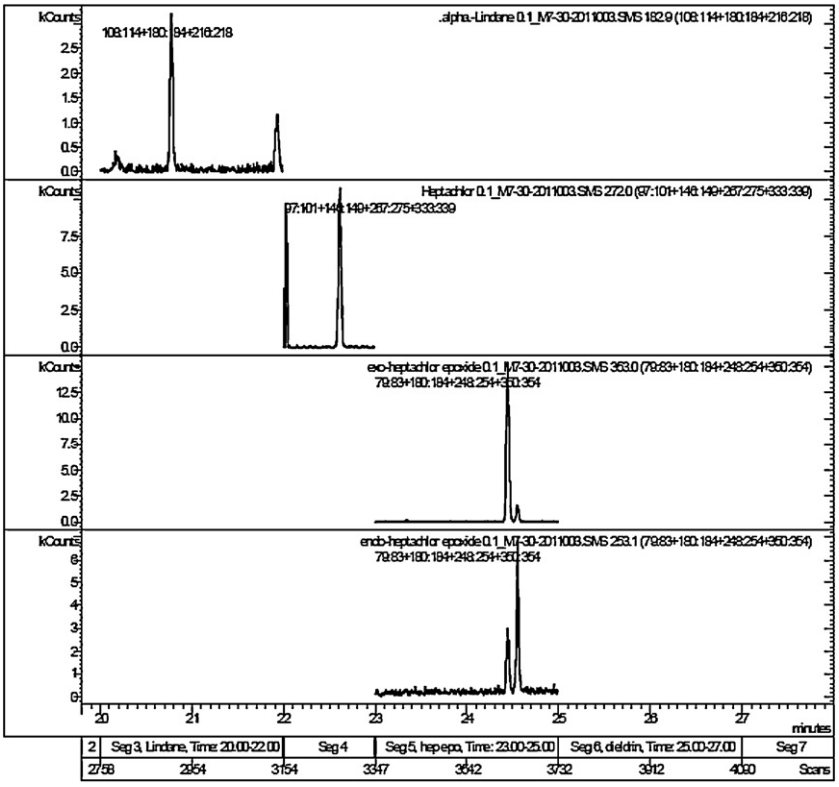



**Fig. 1.** Chromatographic trace, showing the sum of all ions, for each compound at 0.1 μg $L^{-1}$.

extraction. A Varian GC glass insert SPME inlet liner for 1078/1079 injectors (0.8 mm I.D) was used (Sigma Aldrich, Arklow, Ireland). A splitless injection was carried out to help focus the vaporised sample on the column during desorption. The split was initially on at a ratio of 10, and then turned off following injection. After 1 min the split was turned on at a ratio of 10 for four min. The fibre was then baked out at 250 °C for 10 min following desorption in a parallel Varian 1079 injector installed on the instrument to remove non-desorbed analytes and to prevent sample carry over. The PA fibre was replaced after 51 injections to retain sensitivity. The PA fibre was conditioned prior to any analysis for 60 min at 280 °C as recommended by Supelco™ (Sigma Aldrich, Ireland) in the additional Varian 1079 injector installed on the instrument.

### 2.5. GC–MS analysis

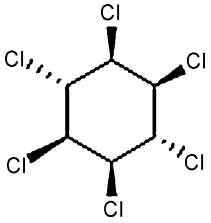
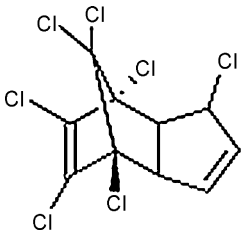
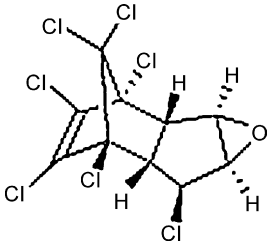
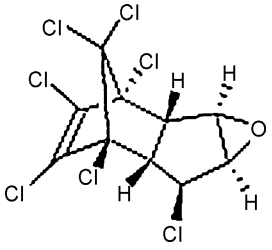
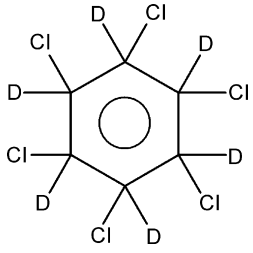
Analysis was carried out on a GC–MS ion trap (Varian CP 3800 and Varian MS Saturn 2000) coupled to a split/splitless Varian 1079 injector operated in splitless mode with a Merlin Microseal™ (Sigma Aldrich, Arklow, Ireland) at 250 °C during chromatographic runs. The use of a Merlin Microseal™ helped reduce the appearance of phthalate plasticisers which would otherwise occur with use of a silicone septum. Separation was achieved using a Zebron ZB-5 capillary column (30 m × 0.25 mm I.D., film thickness 0.25) purchased from Phenomenex (Cheshire, UK). Grade A helium gas was used as the carrier gas (BIP®, Air Products) at a flow rate of 1.0 mL $min^{-1}$. The oven temperature was as follows: 50 °C held for two min and then increased to 280 °C at 8 °C $min^{-1}$. The chromatographic run time was 30.75 min.

Analytes were acquired in electron impact (EI) ionisation mode at 70 eV with SIS (selective ion storage). The MS transfer line, trap, and manifold temperatures were set to 300, 245, and 45 °C, respectively. The retention time of each analyte was identified by injection of individual standards and the MS was segmented using SIS with the analytes unique ions monitored (Table 1). SIS optimised the MS by using only the dominant ions for each compound of interest based on their compound structures. For example heptachlor with ions: 100, 272, 274, 270, and 102 *m/z*. SIS improves sensitivity by discarding ions which may interfere or compete in the MS trap. During SIS, the scan time was 0.4 s, the target total ion count (TIC) was 20,000 counts, the pre-scan ionisation time was 100 μs, the background mass was 49 *m/z*, and the RF dump value was 650 *m/z*. The multiplier offset was 275 V, the emission current 30 μA, and the count threshold at 1 count. *Exo*- and *endo*-heptachlor epoxide were acquired in the same segment because both analytes eluted closely together, which made separating them in two windows impractical without increasing overall GC run time. Fig. 1 shows a typical chromatographic trace at 0.1 μg $L^{-1}$. Peak area was measured for quantitation with the ratio of the sample peak area to that of the internal standard ratio derived for each calibration standard. The deuterated internal standard of α-HCH-$D_6$ was used for all four analytes during calibration and quantification.

### 2.6. Validation

Linearity, repeatability (WLr), specificity, limit of quantification (LOQ), and stability experiments were conducted to confirm that results were reliable and consistent in accordance with EU Council Directive (2002/657/EC) [30]. To test method specificity 20 blank samples were processed with five mL of ultra pure water matrix plus 2.5 g of ≥99.5% NaCl to make sure nothing present could interfere with the compounds of interest. WLr was assessed by a single analyst on three separate days. WLr studies were carried out by analysing water samples fortified at five concentrations ($n$ = 6 at each level): 0.015, 0.03, 0.05, 0.1, and 0.15 μg $L^{-1}$. This

**Table 1**
Compound average retention time ($n = 18$), characteristic ions, and the quantification ions monitored using SIS.

| Analyte | Retention time (min) | Characteristic ions in order of decreasing abundance (*m/z*) | Quantification ion (*m/z*) | Main fragmentation ions (*m/z*) |
|---|---|---|---|---|
| Lindane  | 20.79 | 183, 219, 217, 109, 221 | 183 | 148 + 109 |
| Heptachlor  | 22.62 | 100, 272, 274, 270, 102 | 272 | 100 + 237 |
| *Exo*-heptachlor epoxide  | 24.46 | 81, 353, 355, 351, 357 | 353 | 237 + 81 |
| *Endo*-heptachlor epoxide  | 25.57 | 81, 253, 185 | 253 | 183 + 217 + 135 |
| α-HCH-$D_6$  | 19.53 | 197 | 197 | 148 + 109 |

allows results to be found for each compound with spikes at 0.5, 1.0, and 1.5 times the permitted limit of 0.1 μg $L^{-1}$ for lindane and 0.03 μg $L^{-1}$ for heptachlor, *exo*- and *endo*-heptachlor epoxide. The LOQ is the lowest concentration at which the analyte can be reliably detected. This was determined to be 0.015 μg $L^{-1}$ for each analyte following the analysis of 10 fortified water samples.

### 2.7. Stability

PA fibre longevity over time was determined by continually injecting spiked samples at 0.05 μg $L^{-1}$ until a consistent loss in concentration occurred which was taken as the number of injections a single PA SPME fibre could handle. The calculation of each analytes stability in prepared vials with NaCl over time was carried out by using the solution of the analyte freshly prepared at the time of analysis ($C_o$) and compared with the concentration found at each time point ($C_i$) to determine the percentage of analyte remaining in the vial. Samples were tested every two days until the analytes began to show a loss in concentration.

$$\text{Analyte remaining}(\%) = \frac{C_i \times 100}{C_o}$$

## 3. Results and discussion

### 3.1. Method development

During initial method development four SPME fibres were tested to determine the ideal choice for the compounds of interest.

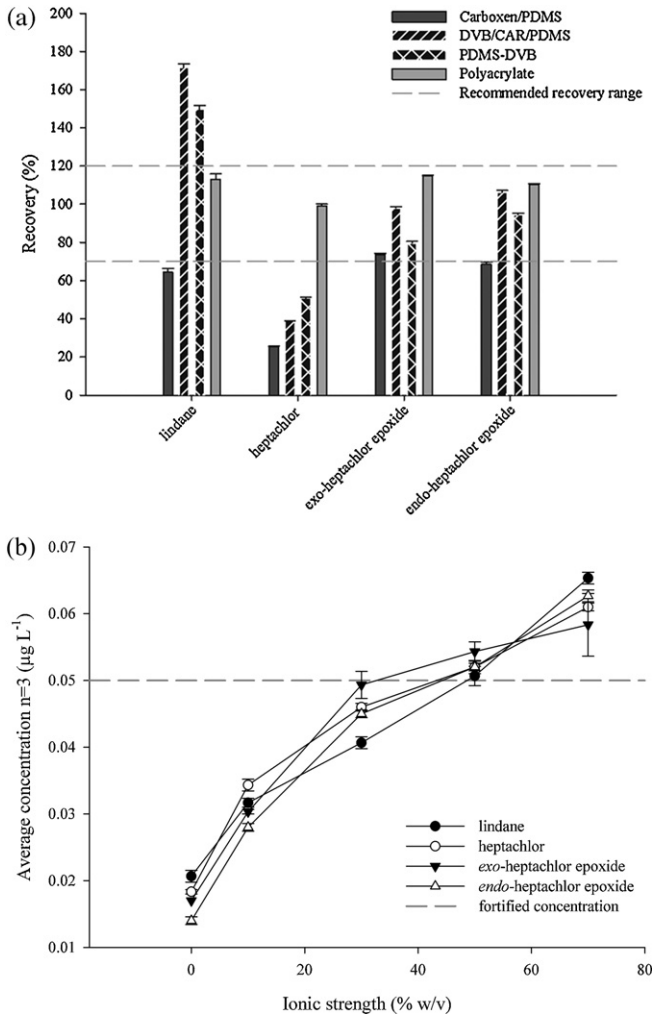



**Fig. 2.** Optimisation of SPME conditions: (a) fibre choice and (b) ionic strength. Error bars represent standard error of the sample mean.

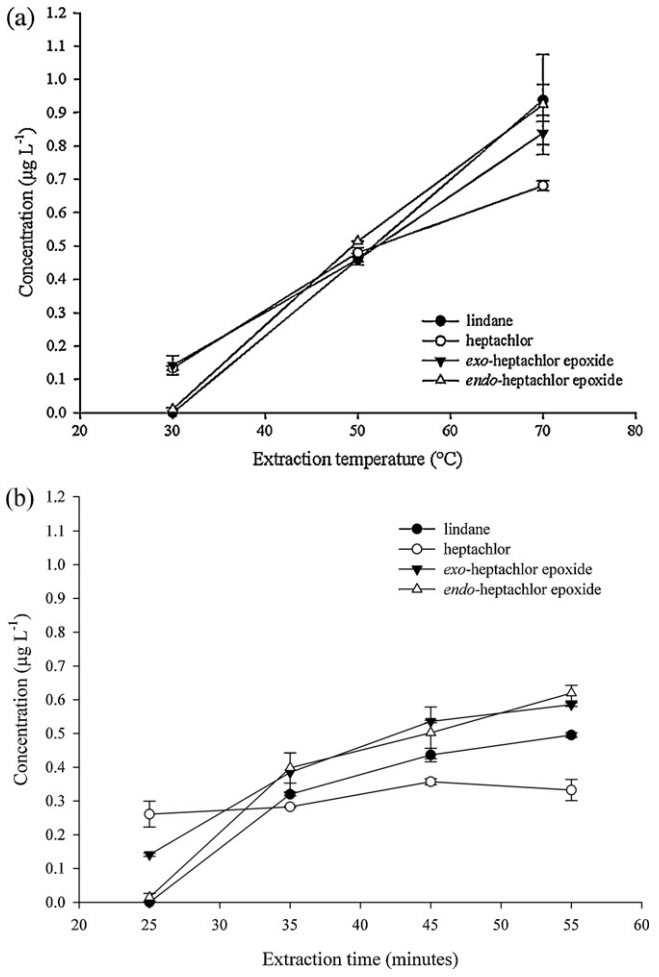



**Fig. 3.** SPME optimisation extraction experiments for (a) temperature and (b) time. Error bars represent standard error of the sample mean.

The best recovery was achieved with a polyacrylate (PA) material for all the compounds (Fig. 2a). It was observed that over time the actual concentration increased during the six replications with PDMS-DVB fibres. PDMS-DVB fibres should be avoided as they will not represent the true concentration in the sample. This carry over may be explained by PDMS-DVB fibres' method of sorption. PDMS-DVB coatings sorb through adsorption which is more permanent than absorption [26].

Salt saturation (0, 10, 30, 50, and 70%, w/v) experiments were also conducted in triplicate using samples fortified at 0.05 $\mu g\,L^{-1}$. The ideal salt saturation for a PA fibre was found to be 50% (w/v) (Fig. 2b). By increasing the salt content, the ionic strength of the water has been increased which allows the analytes to partition more effectively onto the SPME fibre [31].

The extraction temperature and time spent extracting at 250 rpm was optimised by testing spiked samples at 0.5 $\mu g\,L^{-1}$ in duplicate at 30, 50, and 70 °C (Fig. 3a) and for the extraction times 25, 35, 45, and 55 min (Fig. 3b). Optimum extraction temperature was 50 °C which also gave the best precision range (0.1–5.3%) and 45 min time extracting at 50 °C suited all compounds best except lindane which prefers 55 min. Salt saturation, extraction temperature, and extraction time fortified concentrations were over a range of possible concentrations which may occur in environmental groundwaters.

Silanized vials were tested to help improve precision using a 10% (v/v) silane solution in toluene. In six replicates fortified at 0.1 $\mu g\,L^{-1}$, lindane, heptachlor, and endo-heptachlor epoxide were not detected. Only *exo*-heptachlor epoxide was detected with an average concentration of 0.061 $\mu g\,L^{-1}$. Vials were not silanized for validation and application work.

### 3.2. Method validation

#### 3.2.1. Calibration curves

Linearity is the ability to obtain results directly proportional to the sample concentration. A six point calibration curve from 0.015 to 5.0 $\mu g\,L^{-1}$ was analysed in triplicate. Each of the four compounds of interest had a correlation coefficient of 0.9936 or greater when three sets of calibration curves were analysed and the average taken for each. Calibration curves were linear and not forced through the origin. Peak to peak signal-to-noise ratios revealed that all compounds are detectable between the linear range with signal-to-noise ratios greater than 10. Fytianos et al. [32] and Li et al. [33] used signal-to-noise ratios of 3:1 to infer the limit of detection for heptachlor, lindane and heptachlor epoxide whereas this method uses quantitative peak to peak signal-to-noise ratios of 10:1. The retention times of each analyte gathered during the linearity and WLr study ($n = 33$) did not change more than 2.5% and selectivity tests carried out using 20 blank replicates revealed that no other interference peaks appeared at the analytes retention time. The deuterated internal standard was added to each sample to achieve the fortified concentration of 0.1 $\mu g\,L^{-1}$.

**Table 2**
Within laboratory repeatability (WLr) validation results. MAC = maximum allowable concentration in drinking water (0.1 μg L$^{-1}$ for lindane and 0.03 μg L$^{-1}$ for heptachlor, *exo*- and *endo*-heptachlor epoxide).

| Analyte | | Lindane | Heptachlor | *Exo*-heptachlor epoxide | *Endo*-heptachlor epoxide |
|---|---|---|---|---|---|
| Validation levels ($n$ = 6) | 0.5 × MAC | 0.050 | 0.015 | 0.015 | 0.015 |
| (μg L$^{-1}$) | 1.0 × MAC | 0.100 | 0.030 | 0.030 | 0.030 |
| | 1.5 × MAC | 0.150 | 0.050 | 0.050 | 0.050 |
| Recovery (%) | 0.5 × MAC | 101 | 100 | 101 | 101 |
| | 1.0 × MAC | 96 | 101 | 101 | 99 |
| | 1.5 × MAC | 101 | 101 | 100 | 101 |
| Coefficient of variation (%) | 0.5 × MAC | 2.6 | 6.5 | 10.5 | 6.6 |
| | 1.0 × MAC | 1.9 | 5.7 | 6.2 | 4.1 |
| | 1.5 × MAC | 1.4 | 2.7 | 2.3 | 3.3 |
| LOQ (μg L$^{-1}$) | | 0.015 | 0.015 | 0.015 | 0.015 |

### 3.2.2. Repeatability and limit of quantification studies

Recoveries from WLr studies (Table 2) indicate that lindane, heptachlor and *exo*- and *endo*-heptachlor epoxide all had good recoveries spanning the range 96–101%. CV% for lindane, *exo*- and *endo*-heptachlor epoxide, and heptachlor were all less than 10.5% (Table 2). Relative recoveries of 81, 79, and 86% in a study by Faraji and Helalizadeh [21] were found for lindane, heptachlor and heptachlor epoxide, respectively. Precision for these recoveries was less than 7.3% but samples were spiked with uncharacteristically high concentrations of 2 and 10 μg L$^{-1}$. Basheer et al. [22] also spiked samples for validation at high concentrations of 40 μg L$^{-1}$ which is 400 times the EU drinking water standard for individual pesticides.

The LOQ for each analyte was determined to be 0.015 μg L$^{-1}$ based on the first point on the calibration curve. This LOQ is below the limits of 0.1 and 0.03 μg L$^{-1}$ set for lindane and heptachlor residues in drinking water (Table 2).

### 3.3. Stability

Compound stability over time in prepared vials (Fig. 4), calculated as a percentage of the analyte remaining in the vial from the initial concentration on day 1 revealed that heptachlor was the most unstable analyte when stored at room temperature in the dark. *Exo*- and *endo*-heptachlor epoxide started to degrade between day 3 and 5 with *endo*-heptachlor epoxide degrading more quickly than its isomer *exo*-heptachlor epoxide. Lindane was found to be stable for at least 17 days. This study indicates that once vials are prepared they must be analysed by SPME and GC–MS within 24 h otherwise heptachlor, *exo*- and, *endo*-heptachlor epoxide will start to degrade.

Recovery for *exo*- and *endo*-heptachlor epoxide were 107% and 100%, respectively following a 45 min extraction time (Fig. 3b). Recovery for lindane was lower at 87% and for heptachlor was 71%. The reason for heptachlor's reduced recovery in comparison to the other compounds may be because of its relative instability in the environment compared to heptachlor epoxide [13]. Heptachlor in Fig. 4 was the most unstable compound in prepared vials compared to the others. During the fibre choice experiments (Fig. 2a) the lowest recoveries were found for heptachlor using all four SPME fibres tested.

Fibre longevity (Fig. 5) to repeated injections fortified at 0.05 μg L$^{-1}$ showed a drop in sensitivity after 51 injections for lindane, 55 injections for *endo*-heptachlor epoxide, 56 injections for heptachlor and >87 injections for *exo*-heptachlor epoxide. Thus a PA fibre for these compounds analysed together will only last 51 injections including a six-point calibration performed on each SPME PA fibre. Quality control standards (QCs) were ran with every batch of samples to monitor fibre sensitivity, especially in dirty samples with high concentrations as this will vary fibre deterioration.

### 3.4. Application to groundwater samples

The method described was applied to real groundwater samples collected from expertly installed monitoring wells with groundwater levels at 27 m below ground level. Samples were

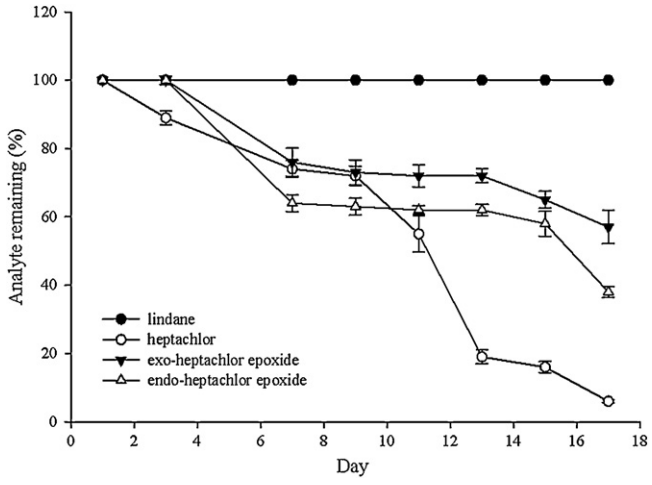



**Fig. 4.** Stability over time of analytes in prepared vials calculated as the percentage of analyte remaining after day 1. Error bars represent standard error of the sample mean.

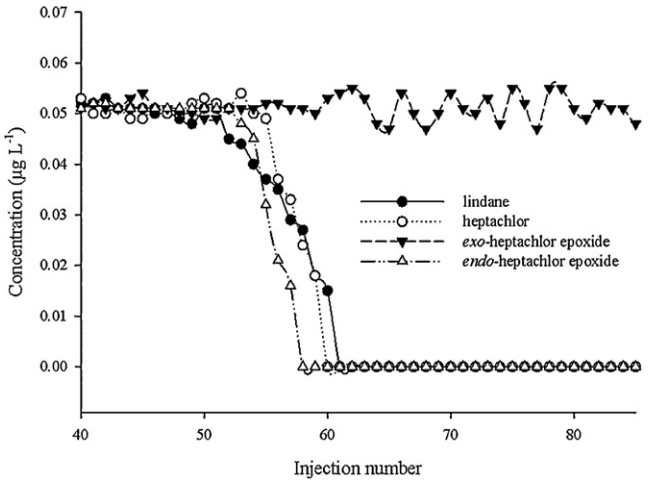



**Fig. 5.** Fibre longevity following repeated injections of fortified samples at 0.05 μg L$^{-1}$.

**Table 3**
Results from groundwater samples.

| Sample | Compound | Retention time (min) | Concentration ($\mu g\,L^{-1}$) | Signal-to-noise |
|---|---|---|---|---|
| a | *Exo*-heptachlor epoxide | 24.448 | 0.037 | 27 |
| b | *Exo*-heptachlor epoxide | 24.448 | 0.046 | 16 |
| c | *Endo*-heptachlor epoxide | 24.597 | 0.033 | 14 |
| d | Lindane | 20.765 | 0.048 | 17 |
| e | Lindane | 20.765 | 0.035 | 24 |

collected into amber glass bottles with chemically inert PTFE lids to contain no air bubbles. Samples were stored at 4 °C and extracted and analysed within 24 h of collection. Table 3 details the positive results found. Detected concentrations ranged from 0.033 to 0.048 $\mu g\,L^{-1}$ for *endo*-heptachlor epoxide and lindane, respectively.

## 4. Conclusions

A less labour intensive method using polyacrylate SPME fibres and GC–MS–SIS in EI mode has been developed and validated in accordance with EU directives and protocols for the identification and quantification of two POPs and two transformation products of heptachlor, which no other method until now has determined. Lindane, heptachlor, *exo*- and *endo*-heptachlor epoxide can be accurately identified and quantified at concentrations between 0.015 and 5.0 $\mu g\,L^{-1}$ which will be able to detect concentrations in accordance with EU Council Directive 98/83/EC permitted limits allowed in drinking water of 0.1 $\mu g\,L^{-1}$ for lindane and 0.03 $\mu g\,L^{-1}$ for heptachlor and its two transformation products. The 17 day stability study indicates that all prepared vials should be analysed within 24 h otherwise degradation of the sample will occur, especially in the case of heptachlor. Polyacrylate fibres for these compounds will last up to 51 injections before fibre affinity losses occur. GC–MS with selective ion storage (SIS) was the technique adopted for quantification and identification. SPME coupled with GC–MS in SIS mode provides a powerful technique for the determination of several POPs covering a range of chemical groups with the ability to achieve detection limits below those set by the EU.

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