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# Analytical Methods for Viable and Rapid Determination of Organochlorine Pesticides in Water and Soil Samples

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## 1. Introduction

Organochlorine pesticides (OCPs) are the potential group of chemicals used to improve agricultural productivity. The extensive use of pesticides to improve agricultural productivity played an important role in the last century. These compounds have been applied for decades in preventing, repelling or mitigating the effects of pests. OCPs are one of the most persistent organic pollutants present in the environment. Although most of OCPs have been banned in many countries because of mutagenic and carcinogenic effects, they and their metabolites are still present in the environment owing to their persistence and lipophilic properties. The toxicity, potential bioaccumulation and non-biodegradability of these compounds represent risks to the environment (FAO/WHO, 1989).

Maximum admissible concentration (MAC) of pesticides and related products for drinking water is  $0.1 \mu\text{g L}^{-1}$  for individual pesticides and  $0.5 \mu\text{g L}^{-1}$  for total concentrations given by the European Union (EU) Drinking Water Directives (EEC, 1980). Additionally, pesticides residue in surface water must be less than  $1\text{--}3 \mu\text{g L}^{-1}$ . Moreover, because of their hydrophobicity and persistence, OCPs accumulate in soils where they are likely to be retained for many years (FAO/WHO, 1989). Therefore, determination and monitoring of OCPs in different environmental matrices are important for environment, especially for human health. Consequently, residue analyses of OCPs in waters and soils by developing analytical procedure continue to be an active area of research in recent years (Santos & Galceran, 2004).

Trace analysis of OCPs in water is usually performed by gas chromatography (GC) combined with a previous an extraction or a pre-concentration step including traditional liquid-liquid extraction (LLE) (Barcelo', 1993, Fatoki & Awofolu, 2003; Tahboub et al., 2005), solid phase extraction (SPE) (Aguilar et al., 1996; 1997), solid phase microextraction (SPME) (Page & Lacroix, 1997; Aguilar et al., 1999; Tomkins & Barnard, 2002; Li et al., 2003; Dong et al., 2005) and the more recently developed liquid phase microextraction under different names, i.e., dispersive liquid-liquid microextraction (DLLME) (Cortada et al., 2009a; Leong & Huang, 2009; Tsai & Huang, 2009), liquid-phase microextraction (LPME) (Huang & Huang, 2007; Farahani et al., 2008), single-drop microextraction (SDME) (Cortada et al., 2009b), polymer-coated hollow fiber microextraction (PC-HFME) (Basheer et al., 2004), stir bar sorptive extraction (SBSE) (Leo'n et al., 2003; Pe'rez-Carrera et al., 2007), ultrasound

assisted emulsification-microextraction (USAEME) (Ozcan et al., 2009a), vortex assisted liquid-liquid microextraction (VALLME) (Ozcan, 2010). Among these methods, LLE and SPE are the oldest procedures for the extraction of OCPs from aqueous matrices. LLE is probably the most widely used method for the extraction of OCPs from aqueous samples (Barcelo, 1993, Fatoki & Awofolu, 2003; Tahboub et al., 2005). However, LLE needs relatively large volumes of organic solvents and samples and it is time-consuming as well as a labor-intensive method, and hazardous to health and environment. The LLE method has some complications such as the formation of stable emulsions. SPE has been used as an alternative method to LLE for the extraction of OCPs from water samples because it uses less solvent and is less time-consuming than LLE. Nevertheless SPE demands a large volume of organic solvents and samples. However, SPE is a relatively expensive method. In this method, analytes may be adsorbed, and complex matrices can cause settling in cartridges (Leong & Huang, 2009; Ozcan et al., 2009a; Quayle et al., 1997). LLE and SPE methods complicate and difficultly in automation. Using large amounts of organic solvents can cause environmental pollution and health hazards for laboratory personel and extra operational costs for waste treatment (Sarafraz-Yazdi & Amiri 2010).

Therefore, in order to overcome disadvantages of these methods, an efficient, fast, easy, economical and comparable sample preparation method such as solid-phase microextraction (SPME) and different modes of liquid-liquid microextraction (LLME), termed as liquid-phase microextraction (LPME) or solvent microextraction (SME) for example single drop microextraction (SDME), dispersive liquid-liquid microextraction (DLLME), ultrasound assisted emulsification-microextraction (USAEME) and vortex assisted liquid-liquid microextraction (VALLME) have been developed in recent years.

Among these methods, SPME is based on the partitioning of analytes between sample matrixes and the polymer-coated fibre. While SPME has some important advantages such as rapid, simple, solvent free, the main disadvantages of SPME method are relatively high price and fragile coating layer of fiber. Fiber also can degrade with time and the partial loss of stationary phase can cause co-elution with the analytes. In addition, sample carry-over has been frequently reported for SPME method (Psillakis et al., 2003). Liquid-liquid microextraction is based on the distribution of the analytes between a microvolume of organic solvent and the aqueous solution (He & Lee, 1997; Jeannot & Cantwell, 1996; 1997). These alternative techniques such as SDME, LPME, DLLME have advantages, such as short extraction time, small volumes of solvent and water requirement, rapid, easy, and low cost. Compared to the SPME, SDME has many advantages including no sample carry-over, wide selection of available solvents, simplicity and ease of use, short pre-concentration time, requiring no conditioning (as is the case with the fibre in the SPME), no need for instrument modification, etc. Nevertheless, these techniques also have some drawbacks. For example, SDME method has difficulty to automate, instability of droplet, and relative low precisions (Xu et al., 2007). In comparison to the traditional LLE and SPE, LPME procedure has many advantages including wide selection of available solvents, low cost, simplicity and ease of use, minimal solvent use, short pre-concentration time and possibility of automation. Furthermore compared to the SPME, LPME has also advantages, such as no sample carry-over, requiring no conditioning, no need for instrument modification, etc. (Khajeh et al., 2006). Nevertheless, some drawbacks, such as instability of droplet and relative low precision were reported for LPME procedure (Xu et al., 2007). DLLME is based on the formation of tiny droplets of the extractant in the sample solution using water-immiscible organic solvent (extractant) dissolved in a water-miscible organic dispersive solvent. The advantages of DLLME could be given as rapid, simple, short extraction time, low cost, high

recovery of analytes. However, general drawbacks of this method are difficult to automate and it requires using a dispersive solvent which usually decreases the partition coefficient of analytes into the extraction solvent (Rezaee et al., 2006; Pena-Pereira et al., 2009).

USAEME procedure combines micro-extraction system and ultrasonic radiation in one step. Ultrasonic radiation is a powerful means for acceleration of various steps in analytical procedure for both solid and liquid samples (Priego-Lopez & Luque de Castro, 2003; Aydin et al., 2006; Tor et al., 2006a; 2006b; Ozcan et al., 2009a; 2009b; 2009c; 2010). USAEME technique leads to an increment in the extraction efficiency in a minimum amount of time (Luque de Castro & Priego-Capote, 2006; 2007). Some other advantages of USAEME are viable, simple, rapid, low cost, and it needs less amount of sample and extraction solvent (Ozcan et al., 2009a; Saleh et al., 2009; Luque de Castro & Priego-Capote, 2007). However, the most important disadvantage of this method is that excessive ultrasound energy may degrade the analytes in water and may cause irreversible damages to the properties of analytes (Luque de Castro & Priego-Capote, 2007; Sanchez-Prado et al., 2008). A novel extraction technique, which is called as vortex-assisted liquid-liquid microextraction (VALLME) has recently been developed. In this method, dispersion of the solvent phase into the aqueous solution has been provided by using vortex mixing and miniaturization approach has been achieved using a micro volume of extraction solvent. VALLME is a fast, repeatable and efficient method and it requires quite small volume of extraction solvent.

The analysis of trace levels of organic pollutants in complex matrices such as soil, sediment usually requires several steps. An extraction step is followed by a clean-up of the extract prior to the chromatographic analysis. Extraction is a critical sample preparation step for the analysis of OCPs in soil samples because these hydrophobic compounds are strongly sorbed to the soil material. Various extraction procedures including soxhlet (Wobst et al., 1999; Fatoki & Awofolu, 2003; Bakan & Ariman, 2004), shaking flask (Kolb et al., 1995; Pozo et al., 2001; Nawab et al., 2003), sonication (Babic et al., 1998; Gonçalves & Alpendurada, 2005; Banjoo & Nelson, 2005; Castro et al., 2001), microwave assisted extraction (MAE) (Camel, 2000; Ericsson & Colmsjo, 2000; Pino et al., 2000; Jayaraman et al., 2001), super critical fluid extraction (SFE) (Reindl & Hofler, 1994; Barnabas et al., 1995; Koinnecke et al., 1997; Benner, 1998; Morselli et al., 1999) and pressured liquid extraction (Lundstedt et al., 2000; Ramos et al., 2000; Richter, 2000) can be used for the extraction of target compounds from soil. Moreover, determination of OCPs in soil can be carried out by using German standard method (DFG S-19 multimethod) (DFG, 1987) and ISO 10382 (ISO, 2002). The preference of each technique mainly depends on the efficiency, recovery, reproducibility, minimal solvent use, simplicity and ease of use. Soxhlet extraction is considered to be the standard method used for the extraction of OCPs from soils. The soxhlet and shaking flask extractions are time consuming and require large volume of organic solvents (Bøwadt et al., 1995; Hartonen et al., 1997; Schantz et al., 1998). Therefore, in order to reduce the extraction time, amount of solvent required, as well as sample amount, new extraction procedures, i.e., supercritical fluid extraction (SFE) (Bøwadt & Hawthorne, 1995), microwave assisted extraction (MAE) (Eskilsson & Björklund, 2000) and accelerated solvent extraction (ASE) (Björklund et al., 2000) etc., have been developed as alternative techniques. More recent procedures, i.e., SFE, MAE and ASE, gave shorter extraction time and reduced solvent consumption because these extraction procedures are working at high temperatures above the boiling point of the solvent. Except for SFE, reconcentration and clean-up steps have to be performed for MAE and ASE procedures. On the other hand, time and cost needed for SFE are quite high as well as for ASE (Berset et al., 1999).

Therefore, nowadays, modern methods have been proposed to solve time and solvent consuming problems as an alternative to traditional methods (Berset et al., 1999). Ultrasonic extraction procedure has lower equipment cost, ease of operation, little or no sample preparation (e.g. wet sediments) and lower extraction temperature, etc. Therefore, it can be also used to extract the target compounds from soil as an alternative to common Soxhlet and shaking flask extraction (Sporring et al., 2005; Aydin et al., 2006; Tor et al., 2006).

Ultrasonication is being used more and more in analytical chemistry, enabling different steps in the analytical process, particularly in sample preparation, such as the extraction of organic and inorganic compounds from different matrices (Ashler et al., 2001; Aydin et al., 2006; Ozcan et al., 2008; Mierzwa et al., 1997). This type of energy is of great help in the pre-treatment of samples as it facilitates and accelerates operations such as the extraction of organic and inorganic compounds. In ultrasound-assisted LLE, it facilitates the emulsification phenomenon and accelerates the mass-transfer process between two immiscible phases. The most widely accepted mechanism for ultrasound-assisted emulsification is based on the cavitation effect. The implosion bubbles generated by the cavitation phenomenon produces intensive shockwaves in the surrounding liquid and high velocity liquid jets. Such microjets can cause droplet disruption in the vicinity of collapsing bubbles and thus, improve emulsification by generating smaller droplet size of the dispersed phase right after disruption (Luque de Castro & Priego-Capote 2006). Submicron droplet-size results in significant enlargement of the contact surface between both immiscible liquids improving the mass-transfer between the phases. Additionally, ultrasonication offers several advantages that make it an ideal method for pre-treating a large number of samples. These advantages include high extraction efficiency, lower equipment costs, ease of operation and lower extraction temperatures, etc. Therefore, in this chapter, the application of ultrasonic extraction procedures for residue analysis of OCPs in water and soil samples was described. The applicability of the ultrasonic extraction was evaluated by comparison with traditional extraction methods (LLE and SPE for water samples, shaking flask, soxhlet extraction and large-scale ultrasonic extraction for soil).

## 2. Aim of the study

Because of the toxicity, potential bioaccumulation and non-biodegradability of OCPs represent risks to the environment. Thus, analysis of different environmental samples for OCPs is of importance for environment health.

At present, more than 60% of registered pesticides and/or their metabolites can be analyzed by using gas chromatography (GC). GC equipped with electron capture detector (ECD) is the most widely used technique especially for the determination of OCPs in different matrices (Santos & Galceran, 2004; Bruner, 1993). Chromatographic analysis usually follows the tedious sample preparation to extract the pollutants from environmental matrices (i.e. soil, sediment, air, water). For the isolation of target compounds from matrices various, extraction and clean-up procedures have been employed. The isolation of OCPs from environmental samples is often difficult and time consuming. The preference of each technique used for the extraction of OCPs from both water and soil samples mainly depends on solvent and time consumption, ease of operation, etc. Therefore, nowadays, modern methods have been proposed to solve time and solvent consuming problems as an alternative to traditional methods. A miniaturisation strategy has been successfully applied on the various extraction procedures, to establish a viable, rapid and easy procedure for

residue analyses of some organic pollutants in soil and sediment samples as well as reducing sample and solvent requirements.

Ultrasound assisted extraction offers several advantages that make it an ideal method for pre-treating a large number of samples. These advantages include high extraction efficiency, lower equipment costs, ease of operation and lower extraction temperatures, etc. Therefore, in this chapter the application of miniaturised ultrasonic extraction procedures for residue analysis of OCPs in water and soil samples was described. The miniaturised ultrasonic extraction applied to the water samples is also called as ultrasound assisted emulsification microextraction (USAEME). The applicability of the miniaturised ultrasonic extraction was evaluated by comparison with traditional extraction methods (shaking flask, soxhlet extraction and large-scale ultrasonic extraction of soil samples, while LLE and SPE of water samples).

### 3. Experimental

#### 3.1 Reagents and solvents

All chemicals used were of analytical grade. OCPs mixed standard including  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -hexachlorocyclohexane (HCH), heptachlor, heptachlor epoxide, dieldrin, aldrin, endrin, endrin aldehyde, endrin ketone, endosulfan I, endosulfan II, endosulfan sulfate, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, methoxychlor were from Accustandard Co. (New Haven, CT, USA). Solvents of residue grade purity including acetone, dichloromethane, chloroform, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, *n*-hexane, methanol, ethylacetate were obtained from Merck Co. (Darmstadt, Germany). Sodium chloride and sodium sulfate were also from Merck Co. Octadecyl ( $C_{18}$ ) SPE cartridges were obtained from J&T Baker (Deventer, Holland). Alumina 90 active, neutral, [(0.063–0.200 mm), (70–230 mesh ASTM)] was also from Merck Co. Standard stock solution 10 mg L<sup>-1</sup> of mixed OCPs was prepared in methanol. All solutions were stored in the dark at 4 °C. Working solutions were prepared by dilution of standard stock solution with distilled water.

#### 3.2 Chromatographic analysis

The determination of the OCPs was performed by GC/ $\mu$ -ECD (Agilent Technologies, CA, USA). The features and operating conditions of GC/ $\mu$ -ECD system were as follows: GC Agilent 6890 N installed with HP-5 5% phenylmethyl siloxane fused silica capillary column (30 m length, 0.32 mm i.d. and 0.25  $\mu$ m film thickness). The split/splitless injector was set at 280 °C and operated in the splitless mode (purge delay 1 min, purge flow 30.1 mL min<sup>-1</sup>). Detector temperature was set at 320 °C. The injection was performed by an Agilent 7683 B series automatic injector. The temperature program was as follow: initial column temperature 60 °C, 40 °C min<sup>-1</sup> to 160 °C, 5 °C min<sup>-1</sup> to 300 °C, hold at 300 °C for 5 min (run time 35.5 min). Helium (purity 99.999%) was used as carrier gas at flow rate of 2.5 mL min<sup>-1</sup>.

#### 3.3 Clean-up procedure

The activation and deactivation of the column sorbent material, aluminum oxide, was performed as follows. The aluminum oxide was activated at 210 °C for 4 h. It was allowed to cool down in a desiccator and then deactivation and homogenization were carried out by adding certain amounts of deionized water (5%) and shaking the sorbents in a horizontal shaker at 210 rpm for 2 h. The preparation of the traditional clean-up column filled with 10 g of deactivated column sorbent material was described in a previous paper (Tor et al., 2006).

The clean-up column, length of 30 cm and 1 cm of internal diameter, was prepared according to slurry packing technique (Jaouen-Madoulet et al., 2000). The extract, reduced in volume to 1 mL, was transferred quantitatively onto the top of the column. The elution of OCPs was carried out with 100 mL of *n*-hexane/ethylacetate (1/1, v/v), then the extract was concentrated to exactly 1 mL using a rotary evaporator (Buchi B-160 Vocabox, Switzerland) and nitrogen stream prior to GC/ $\mu$ -ECD analysis. The micro-scale clean-up column consisted of a pasteur pipette, length of 10 and 0.5 cm internal diameter, fitted at its base with a plug of glass wool. 0.5 g aliquot of 5% deactivated aluminium oxide was filled into the pasteur pipette and conditioned with 5 mL of *n*-hexane. After miniaturized ultrasonic extraction, the extract was reduced in volume to 300  $\mu$ L and it was transferred top of the column. The target compounds were eluted from the pipette under gravity (flow-rate of approximately 2 drop s<sup>-1</sup>) with 5 mL of *n*-hexane/ethylacetate (7/3, v/v). The eluate was concentrated to 300  $\mu$ L prior to GC/ $\mu$ -ECD analysis.

### 3.4 Liquid-liquid extraction

Liquid-liquid extraction (LLE) procedure was adopted from US EPA Method 3510C (US EPA, 1996). 200 mL of water sample was placed in a 250 mL capacity of separatory funnel. The extraction was carried out three times with 20 mL of dichloromethane. The extracts were combined and dried with anhydrous sodium sulfate. The resulting extract was concentrated to exactly 1 mL using a rotary evaporator (Buchi B-160 Vocabox, Flawil 1, Switzerland) and gentle nitrogen stream. Then, GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.5 Solid-phase extraction

SPE procedure was carried out as described by Aydin et al. (2004). Octadecyl (C<sub>18</sub>) SPE cartridge was used for the extraction of OCPs from water sample. The cartridge was consecutively washed with 10 mL of methanol and 8 mL of *n*-hexane/ethyl acetate (5/3, v/v). Then, it was conditioned with 10 mL of methanol and 2×5 mL of distilled water. 200 mL of water sample was passed through the cartridge under vacuum. After the cartridge was dried for 10 min by maintaining vacuum, elution of OCPs from the cartridge was carried out with 10 mL of *n*-hexane/ethyl acetate (7/3, v/v). The extract was dried with sodium sulfate and concentrated to exactly 1 mL by a rotary evaporator and under gentle nitrogen stream. Then, GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.6 Shake flask extraction

For shake flask extraction, a 10 g of soil sample was suspended in 50 mL of petroleum ether/acetone mixture (1/1, v/v) and shaken on a horizontal shaker for 12 h. Then, the extract was filtered and concentrated to exactly 1 mL by using the rotary evaporator and nitrogen stream, respectively (Tor et al., 2006; Aydin et al., 2006). The concentrated extract was transferred onto the traditional clean-up column and elution was performed as described in Section 3.3. GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.7 Soxhlet extraction

For soxhlet extraction, a 10 g of soil sample was put into the extraction thimble and extracted with 150 mL of petroleum ether/acetone mixture (1/1, v/v) for 18 h (Tor et al., 2006; Aydin et al., 2006). The extract was reduced to exactly 1 mL using the rotary

evaporator and under a gentle stream of nitrogen. The concentrated extract was transferred onto the traditional clean-up column and elution was performed as described in Section 3.3. GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.8 Large-scale ultrasonic extraction

Ultrasonic extraction of 10 g of soil sample was performed twice by using 25 mL of petroleum ether and acetone mixture (1/1, v/v) for 20 min (Tor et al., 2006a). After extraction steps, extracts were filtered and combined in a round bottom flask. The extract was reduced to exactly 1 mL using the rotary evaporator and under a gentle stream of nitrogen. The concentrated extract was transferred onto the traditional clean-up column and elution was performed as described in Section 3.3. GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.9 Miniaturised ultrasonic extraction of OCPs from water samples

A 10 mL water sample was placed in a 10 mL glass-centrifuge tube. As an extraction solvent, 200  $\mu$ L chloroform was added into the water sample and mixed. The resulting mixture was immersed into an ultrasonic bath (frequency 35 kHz, 320W, Super RK 510, Sonorex, Bandelin, Germany) for 15 min at 25 °C. During the sonication, the solution became turbid due to the dispersion of fine chloroform droplets into the aqueous bulk. The emulsification phenomenon favoured the mass-transfer process of OCPs from the aqueous bulk to the organic phase. The emulsion was centrifuged at 4000 rpm for 5 minutes to disrupt the emulsions and separate the solvent from the aqueous phase. After centrifugation, extraction solvent was removed from the bottom of the tube by using a 250  $\mu$ L Hamilton syringe (Hamilton Bonaduz AG, Switzerland) and transferred into the microvial. Then, GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.10 Miniaturised ultrasonic extraction of OCPs from soil samples

A 0.5 g soil sample was sonicated three times for 5 minutes with 5 mL of mixture of acetone-petroleum ether (1/1, v/v) in the ultrasonic bath. The extracts were combined and were filtered by using Whatman filter paper. The filtrates were reduced to 1 mL with the rotary evaporator (Buchi B-160 Vacobox, Switzerland) and adjusted to exactly 300  $\mu$ L by using a gentle nitrogen stream. The concentrated extract was transferred onto the micro-scale clean-up column and elution was performed as described in Section 3.3. Then, GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

### 3.11 Real water and soil samples

The efficiency of the ultrasonic extraction of OCPs from different water samples (i.e., tap water, well water, lake water, domestic and industrial wastewater samples) was compared with traditional LLE and SPE procedures. Tap water was obtained from the laboratory and well water came from deep-ground water in Konya (Turkey). Lake water was taken from Cavuscugol in Ilgın (Turkey). The domestic and industrial wastewater samples were taken from the sewage system in residential area and industrial zone in Konya (Turkey), respectively. All samples were collected free of air bubbles in glass containers and they were stored in the dark at 4 °C. Tap and well water samples were analysed without previous treatment or filtration. The lake water, domestic and industrial wastewater samples were filtered through a membrane filter with 0.45  $\mu$ m pore size before the extraction procedures.

The efficiency of the ultrasonic extraction of OCPs from the real soil samples was also compared with traditional soxhlet, shake-flask and large-scale ultrasonic extraction procedures on the real soil samples. Real soil samples were also obtained from the Department of Soil, Agricultural Faculty of Selcuk University (Konya, Turkey). The textures of the soil samples were as follows. Sample A, sand: 42.2%, silt: 31.5%, clay: 24.5, organic matter: 1.80%, pH (0.01 M CaCl<sub>2</sub>): 7.2 and maximum water capacity: 20.4%. Sample B, sand: 49.2%, silt: 32.3%, clay: 18.5%, organic matter: 1.90%, pH (0.01 M CaCl<sub>2</sub>): 6.5, and maximum water capacity: 19.6%. Sample C, sand: 39.9%, silt: 35.0%, clay: 23.8%, organic matter: 1.36%, pH (0.01 M CaCl<sub>2</sub>): 7.3, and maximum water capacity: 24.1%.

## 4. Results and discussions

### 4.1 Water analysis

The recovery experiments were carried out for the evaluation of the miniaturised ultrasonic extraction efficiency of selected OCPs in water samples. After choice of the most suitable solvent and solvent volume, several other parameters including extraction time, centrifugation time and ionic strength of the water sample were optimized. The applicability of ultrasonic solvent extraction procedure was also compared with LLE and SPE methods on the real water samples.

At the beginning of the experiments, the extraction efficiency of dichloromethane, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, chloroform and bromoform was determined. The choice of extraction solvent is critical for developing an efficient ultrasonic solvent extraction procedure since physico-chemical properties of the solvent govern the emulsification phenomenon, and consequently, the extraction efficiency. Moreover, the extraction solvent should have good affinity for target compounds and it should have excellent gas chromatographic behavior. 10 mL aliquots of distilled water including 2 µg L<sup>-1</sup> of each OCP were extracted by using 100 µL of each solvent in ultrasonic bath for 5 min at 25 °C. During the sonication, the solution became turbid due to the dispersion of fine solvent droplets into the aqueous bulk. The emulsification phenomenon favored the mass-transfer process of OCPs from the aqueous bulk to the organic phase. Emulsification was observed in all cases with the exception of dichloromethane. Dichloromethane was completely dissolved in the aqueous solution. The results revealed that chloroform was of the highest extraction efficiency among the examined solvents.

In the second set of experiments, the optimum volume of solvent was determined. The main effect of the ultrasound in LLE is that the fragmentation of one of the phases to form emulsions with submicron droplet size that enormously extend the contact surface between both liquids (Abismail et al., 1999). Therefore, it is expected that increasing the volume of chloroform from 50 to 300 µL increases the number of submicron droplet. Hence, the higher mass-transfer or extraction efficiency is obtained. This optimization experiment was carried out using chloroform, which gave the highest recovery for the pesticides studied. In order to determine the optimum volume of chloroform, 10 mL fortified distilled water was extracted by means of ultrasound for 5 min with 50, 100, 200 and 300 µL of chloroform. 50 µL chloroform were completely dissolved in the aqueous solution. The results showed that the recoveries increased with chloroform volume from 100 to 200 µL. Then, a decrease in the recoveries was generally observed when the solvent volume was increased to 300 µL. Increasing the extraction solvent (chloroform) volume from 100 to 200 µL resulted in higher

extraction efficiency. However, increasing the solvent volume 300  $\mu\text{L}$  caused a decrease in the response of the detector, and the unfavorable effect of larger solvent volume was because of a dilution effect of the analytes in the resulting organic phase. Therefore, in the present study, 200  $\mu\text{L}$  of chloroform was selected for further optimization experiments.

After choice of chloroform and 200  $\mu\text{L}$  as the optimum extraction solvent and extraction solvent volume, respectively, several other factors affecting the ultrasonic extraction procedure, such as extraction time (denoted as factor 1), centrifugation time (denoted as factor 2) and ionic strength of the sample (denoted as factor 3) were optimized by using a  $2^3$  factorial experimental design. The corresponding levels (low and high level) for factors 1–3 were 5 and 15 min, 5 and 10 min, 0 and 10%, respectively. All the experiments were performed in duplicate and randomized. After each extraction, the emulsion was centrifuged for 5 min at 4000 rpm. Then, extraction solvent was removed from the bottom of the tube by using a 250  $\mu\text{L}$  syringe and transferred into the micro vial. Then, GC/ $\mu$ -ECD analysis was performed as described in Section 3.2.

After processing the data by analysis of variance (ANOVA) using Tool Pak in Microsoft Excel, the ANOVA tables were constructed to test the significance of the effect of each factor on the extraction efficiency. At significance level of 5%, the factor with *F*-value over critical *F*-value (5.318) has a significant effect on the extraction efficiency.

As it is seen in Table 1, for all compounds, the significant parameters were extraction time (factor 1) and ionic strength of the sample (factor 3). However, centrifugation time (factor 2) was not significant. Additionally, interactions between the extraction time and centrifugation time (factor 1 and 2), between the extraction time and ionic strength (factor 1 and 3) were found to be significant. Lastly, interaction between the centrifugation time and ionic strength (factor 2 and 3) was also significant.

Time plays an important role in the emulsification and mass-transfer phenomena. Extraction time has a positive sign, so 15 min is better than 5 min for the extraction. Like SPME, liquid-liquid micro-extraction procedures are processes dependent on equilibrium rather than exhaustive extraction (Zhao & Lee, 2001; Tor & Aydin, 2006). The amount of analyte extracted at a given time depends upon the mass transfer of analyte from the aqueous phase to the organic solvent phase. This procedure requires a period of time for equilibrium to be established. For present study, it was observed that the recoveries increased with increasing extraction time from 5 to 15 min. Therefore, 15 min was chosen as the extraction time for further studies.

Centrifugation was required to break down the emulsion and accelerate the phase-separation process. As a result, increasing centrifugation time does not influence the extraction efficiency. Thus, 5 min was selected as the centrifugation time to get a satisfactory biphasic system.

Ionic strength of the sample had negative sign for the studied OCPs. As is well known, ionic strength affects the partitioning coefficients of analytes between an aqueous and organic phase. On the other hand, as the ionic strength of the medium increases, the viscosity and density of the solution increase. This causes a diminishing in the efficiency of the mass-transfer process and, consequently, the extraction efficiency of the procedure (Regueiro et al., 2008). Additionally, the ultrasound waves can be absorbed and dispersed in a viscous medium as calorific energy; thus, the cavitation process could be withdrawn reducing the emulsification phenomenon (Mason & Lorimer, 2002). In this study, an increase in the ionic strength of the sample from 0 to 10% decreased the extraction efficiency. Therefore, no sodium chloride was added to the samples for further studies.

| Experiment no | Codified parameters |          |          | No codified parameters |          |          | Average recovery (%) |
|---------------|---------------------|----------|----------|------------------------|----------|----------|----------------------|
|               | Factor 1            | Factor 2 | Factor 3 | Factor 1               | Factor 2 | Factor 3 |                      |
| 1-9           | -                   | -        | -        | 5                      | 5        | 0        | 93                   |
| 2-10          | +                   | -        | -        | 15                     | 5        | 0        | 98                   |
| 3-11          | -                   | +        | -        | 5                      | 10       | 0        | 90                   |
| 4-12          | +                   | +        | -        | 15                     | 10       | 0        | 98                   |
| 5-13          | -                   | -        | +        | 5                      | 5        | 10       | 64                   |
| 6-14          | +                   | -        | +        | 15                     | 5        | 10       | 65                   |
| 7-15          | -                   | +        | +        | 5                      | 10       | 10       | 70                   |
| 8-16          | +                   | +        | +        | 15                     | 10       | 10       | 70                   |

Factor 1, extraction time, Factor 2, centrifugation time, Factor 3, ionic strength of the sample

Table 1. Design matrix for factorial design and average recoveries of OCPs for the effect of parameters on the miniaturised ultrasonic extraction procedure (Ozcan et al., 2009a).

In addition, interaction between factor 1 and 2 was positive and interactions between factor 1 and 3 and factor 2 and 3 were negative. According to the results, the optimum conditions for miniaturised ultrasonic extraction of OCPs from water were chosen as follows: for chloroform as extraction solvent, solvent volume, 200  $\mu\text{L}$ ; extraction time, 15 min without addition of sodium chloride at 25  $^{\circ}\text{C}$ ; and centrifugation time, 5 min.

The results of recoveries for the fortified distilled water with three different fortification levels (level 1, 0.5  $\mu\text{g L}^{-1}$ ; level 2, 2  $\mu\text{g L}^{-1}$ ; level 3, 5  $\mu\text{g L}^{-1}$ ) were given in Fig. 1. The repeatability of the proposed method, expressed as relative standard deviation (RSD), was found to vary between <1 and 9% for the fortified water samples.

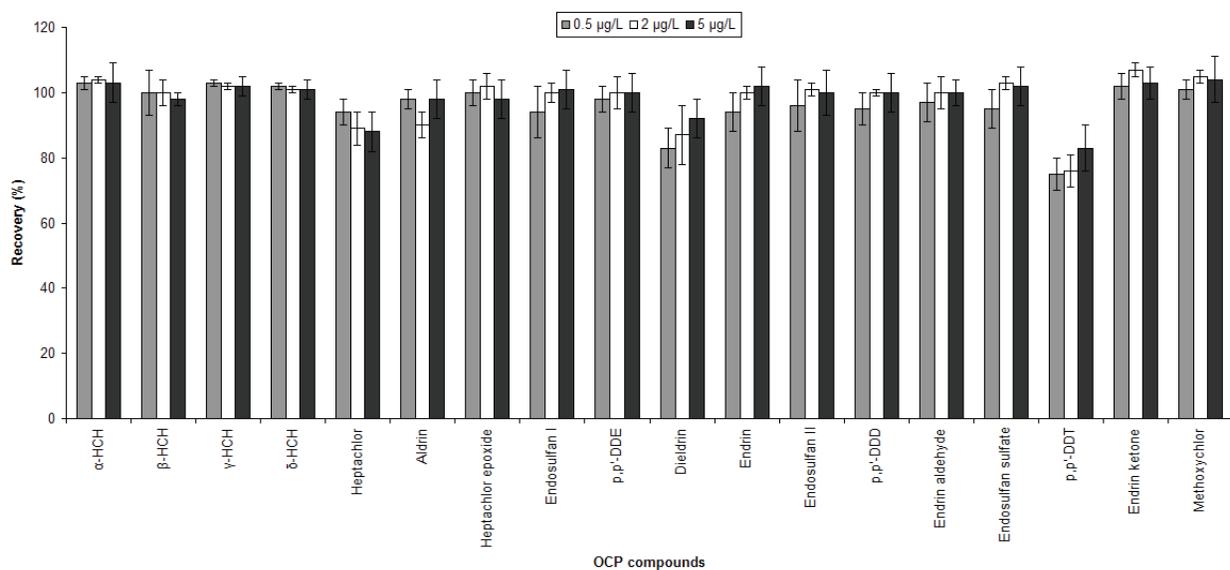


Fig. 1. Recoveries of OCPs in spiked distilled water with three fortification levels using miniaturised ultrasonic extraction method [ $n=8$ ] (Extraction conditions; extraction solvent: chloroform, extraction time: 15 min, sample volume: 10 mL, extraction solvent volume: 200  $\mu\text{L}$ , centrifugation time: 5 min, ionic strength: 0%, ambient temperature: 25  $^{\circ}\text{C}$ )

According to fortification level 1 ( $0.5 \mu\text{g L}^{-1}$ ), recoveries ranged from  $75 \pm 5\%$  to  $103 \pm 2\%$ . Comparable recoveries were also obtained from fortification levels 2 ( $2 \mu\text{g L}^{-1}$ ) and 3 ( $5 \mu\text{g L}^{-1}$ ). When statistical evaluation was carried out between recoveries of OCPs from fortification level 1 and level 2, no significant differences ( $p > 0.05$ ) were observed. Additionally, no significant differences were observed when the same statistical evaluations were carried out between fortification levels 1–3 and 2–3. This indicates that developed miniaturised ultrasonic extraction method (in other word, USAEME method) was of considerable efficiency in extracting OCPs from water samples.

The validation of the miniaturised ultrasonic extraction procedure was carried out using both fortified distilled water and fortified real water and wastewater samples. In addition, the efficiency of the method was also compared with traditional LLE and SPE techniques on the fortified real water samples. The recoveries were given in Figs. 2 and 3, which indicated that the recoveries of examined OCPs were higher than 78% with R.S.D. below 9%. Analyses of real water samples showed that sample matrices had no adverse effect on the efficiency of the miniaturised ultrasonic solvent extraction procedure.

When recoveries of OCPs were gauged against absolute limits of 70% and 130% (US EPA, 1995) it was seen that method gave satisfactory results. The efficiency of the miniaturised ultrasonic extraction was also compared with those involving traditional LLE and SPE method on the same fortified real samples. As seen in Fig. 2 and Fig. 3, the method gave comparable results with traditional LLE and SPE methods. However, it should be emphasized that the ultrasonic extraction is not time-consuming procedure and it is not necessary a re-concentration step prior to the GC analysis. Furthermore, it needs much lower volumes of solvent and water sample than the traditional LLE and SPE techniques.

#### 4.2 Soil analysis

The recovery experiments were carried out for optimization of an miniaturised ultrasonic extraction of OCPs from soil samples. The factors affecting the performance of ultrasonic extraction (i.e., amount of sample, volume of extraction solvent and number of extraction step) were optimized by using a  $2^3$  factorial experimental design. The applicability of the ultrasonic extraction was tested by a comparison with conventional soxhlet, shake flask and large-scale ultrasonic extraction of real soil samples with spiked OCPs.

Different solvents with a wide polarity range such as *n*-hexane, ethyl acetate, acetone and a mixture of petroleum ether and acetone (1/1, v/v) were examined for the optimization of large-scale ultrasonic extraction of OCPs from soil (Tor et al., 2006a). The mixture of petroleum ether and acetone (1/1, v/v) gave the highest recoveries followed by acetone, ethyl acetate and *n*-hexane in ultrasonic extraction. Therefore, the mixture of petroleum ether and acetone (1/1, v/v) was used as extraction solvent for the optimization experiments.

After choice of the mixture of petroleum ether and acetone (1/1, v/v) as the optimum extraction solvent, several other factors affecting the ultrasonic extraction procedure, such as amount of sample (denoted as factor 1), volume of extraction solvent (denoted as factor 2) and number of extraction step (denoted as factor 3) were optimized by using a  $2^3$  factorial experimental design. The corresponding levels (low and high level) for factors 1–3 were 0.5 and 1.5 g, 2 and 5 mL, 1 and 3, respectively. All the experiments were performed in duplicate and randomized. After processing the data by ANOVA, the ANOVA tables were constructed to test the significance of the effect of each factor on the extraction efficiency. At

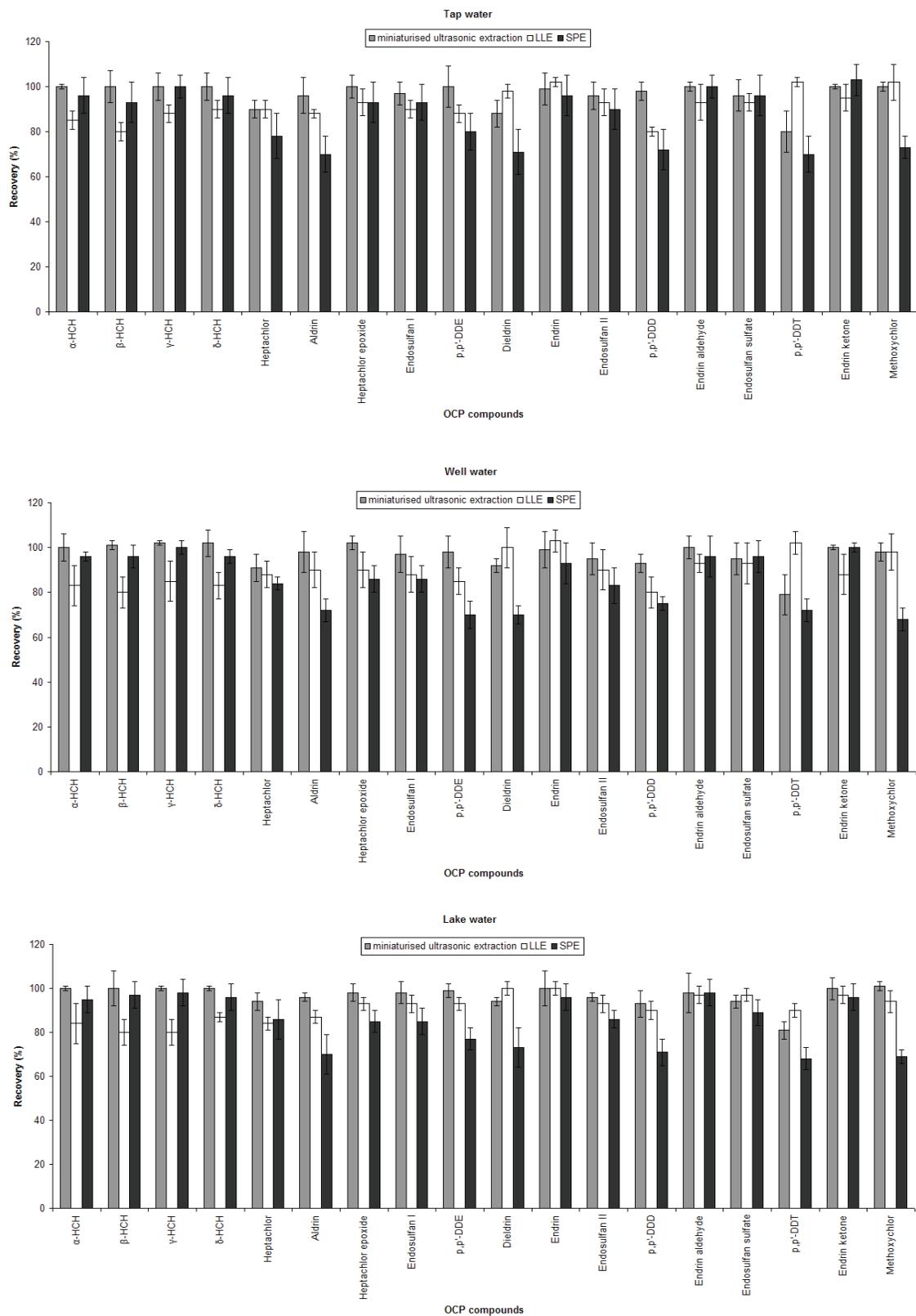


Fig. 2. Comparison of extraction efficiency of the miniaturised ultrasonic extraction method with LLE and SPE for OCPs in fortified real water (tap, well and lake) samples (fortification concentration for each compound:  $2 \mu\text{g L}^{-1}$ ), [ $n=4$ ].

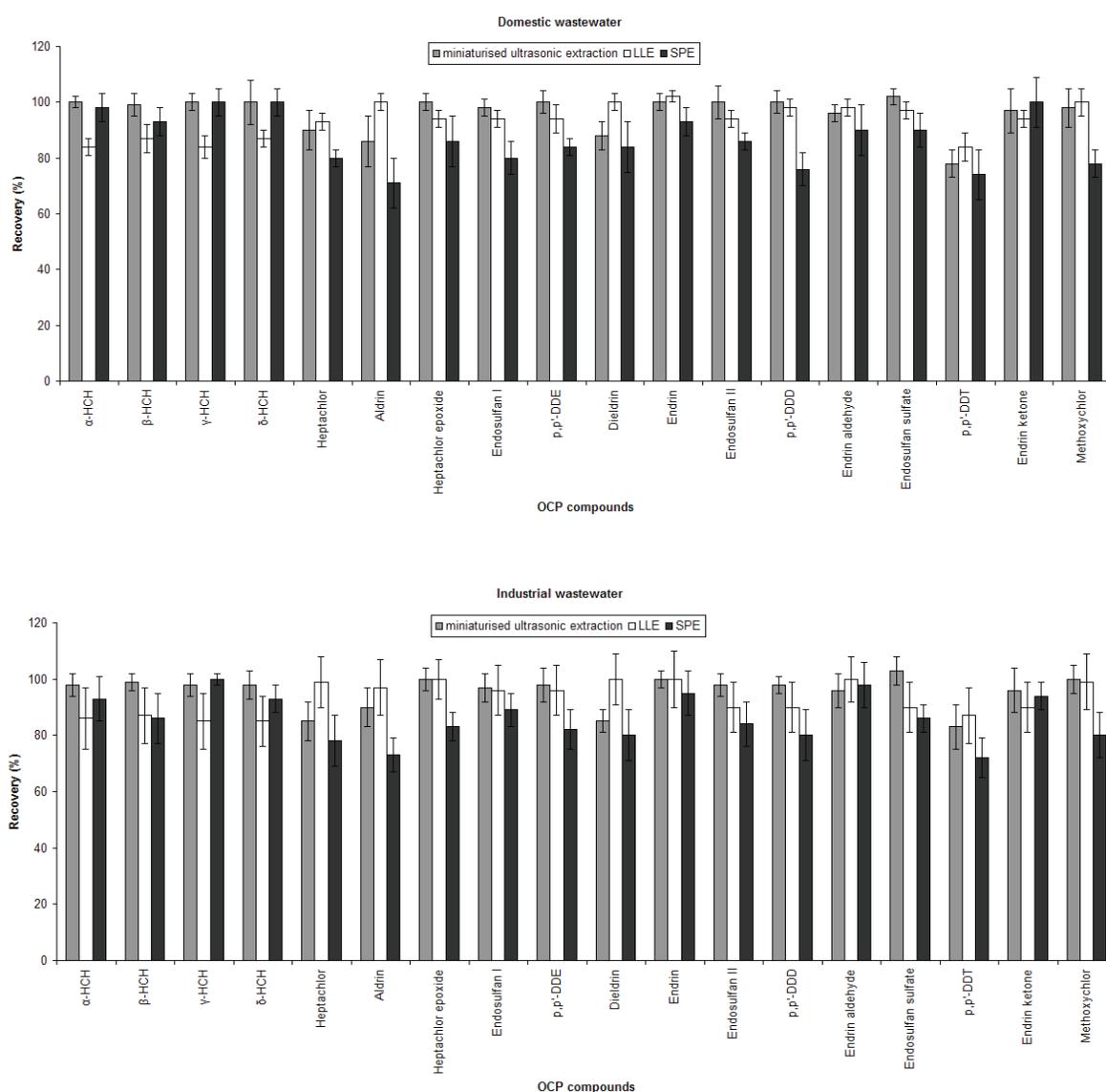


Fig. 3. Comparison of extraction efficiency of the miniaturised ultrasonic extraction method with LLE and SPE for OCPs in fortified real wastewater (domestic and industrial) samples (fortification concentration for each compound:  $2 \mu\text{g L}^{-1}$ ), [ $n=4$ ].

significance level of 5%, the factor with  $F$ -value over critical  $F$ -value (5.318) has a significant effect on the extraction efficiency.

0.5 g of soil sample was sonicated for 5 min with 5 mL of petroleum ether and acetone mixture (1/1, v/v) in an ultrasonic bath. The extraction was repeated three times. After each extraction, extracts were collected in a pointed flask and reduced in volume to 300  $\mu\text{L}$  by a gentle nitrogen stream. Then clean-up procedure and GC/ $\mu$ -ECD analysis were performed as described in Sections 3.3. and 3.2., respectively.

As it is seen in Table 2, for all compounds, the significant factors were sample amount, solvent volume and number of extraction. Additionally, interactions between the sample amount and solvent volume and between the sample amount and number of extraction were found to be significant. Lastly, interaction between the solvent volume and number of extraction was also significant.

Sample amount negatively affected the extraction of all OCPs. It is expected that high sample amount may require longer sonication time needed for the extraction of all OCPs from soil. In other words, fixed sonication time (5 min) was insufficient for extraction of 1.5 g of sample. Another reason may be that 2 mL of extraction solvent is not adequate for completely extraction of OCPs from 1.5 g of soil sample. Hence, 0.5 g of sample is better than 1.5 g for the extraction of OCPs with 2 mL of solvent and 5 min of sonication time.

| Experiment no | Codified parameters |          |          | No codified parameters |          |          | Average recovery (%) |
|---------------|---------------------|----------|----------|------------------------|----------|----------|----------------------|
|               | Factor 1            | Factor 2 | Factor 3 | Factor 1               | Factor 2 | Factor 3 |                      |
| 1-9           | -                   | -        | -        | 0.5                    | 2        | 1        | 36                   |
| 2-10          | +                   | -        | -        | 1.5                    | 2        | 1        | 20                   |
| 3-11          | -                   | +        | -        | 0.5                    | 5        | 1        | 66                   |
| 4-12          | +                   | +        | -        | 1.5                    | 5        | 1        | 47                   |
| 5-13          | -                   | -        | +        | 0.5                    | 2        | 3        | 82                   |
| 6-14          | +                   | -        | +        | 1.5                    | 2        | 3        | 60                   |
| 7-15          | -                   | +        | +        | 0.5                    | 5        | 3        | 93                   |
| 8-16          | +                   | +        | +        | 1.5                    | 5        | 3        | 59                   |

Factor 1, sample amount, Factor 2, solvent volume, Factor 3, number of extraction step

Table 2. Design matrix for factorial design and average recoveries of OCPs for the effect of parameters on the miniaturised ultrasonic extraction procedure (Ozcan et al., 2009d).

Solvent volume had positive sign. 5 mL is better than 2 mL for the extraction. In soil and sludges, OCPs are adsorbed on or in aggregates. Namely, 5 mL of extraction solvent is of more capability than 2 mL for disintegration of the soil aggregates and extraction of OCPs from soil. Number of extraction had also positive sign for all studied OCPs. Increasing the number of extraction step also increased the extraction efficiency. Thus, recoveries obtained from three times extraction are higher than those from single step extraction. As a result from experimental factorial design, optimum conditions for ultrasonic extraction of OCPs from soil were as follows: sample amount: 0.5 g; solvent volume: 5 mL mixture of acetone-petroleum ether (1/1, v/v) and number of extraction step: 3, with a 5 min sonication.

The optimum extraction procedure was examined by using of three different fortification levels (levels 1, 25  $\mu\text{g kg}^{-1}$ ; level 2, 50  $\mu\text{g kg}^{-1}$ ; level 3, 100  $\mu\text{g kg}^{-1}$ ). The results of recoveries were given in Fig. 4. According to fortification level 1, recoveries ranged from 86 ( $\pm 1$ )% to 104 ( $\pm 4$ )%. Comparable recoveries were also obtained from fortification levels 2 and 3 (see Fig. 4). When statistical evaluation was carried out between quantities of OCPs extracted

from fortification levels 1 and 2, no significant differences ( $p > 0.05$ ) were observed. Moreover, the same statistical evaluations were carried out between fortification levels 1-3 and 2-3, no significant differences were observed. This indicated that optimized ultrasonic solvent extraction was of considerable efficiency in order to extract OCPs from soil sample.

The applicability of the miniaturised ultrasonic extraction method to the real soil samples was investigated by comparing with soxhlet, shake flask and large-scale ultrasonic extraction method. The analyses for three different soil samples were carried out. Soil sample A, B and C were spiked with OCPs (spike level for each compound:  $50 \mu\text{g kg}^{-1}$ ) and analysis was performed by using miniaturised ultrasonic solvent extraction, soxhlet extraction, shake flask extraction and large-scale ultrasonic extraction. The results are given in Fig. 5.

As seen in Fig. 5, miniaturised ultrasonic extraction gave comparable results with especially soxhlet and large-scale ultrasonic extraction method. In addition, extraction efficiency of the proposed procedure is generally higher than that of shaking flask extraction. As a results, when recoveries of OCPs for the ultrasonic extraction were gauged against absolute limits of 70% and 130% (US EPA, 1995), it was seen that proposed miniaturised method gave satisfactory results.

Soxhlet and shake flask extractions have been the traditional methods used for extraction of OCPs from soils (ISO, 2002). The main disadvantages of these methods are that there are needs for more volume of solvent, long time for extraction, reconcentration and clean-up steps (Bøwadt et al., 1995; Hartonen et al, 1997). Ultrasonication allows an intensive contact between soil particles and solvent and it reduces the extraction time. Therefore, miniaturised ultrasonic extraction can be used to extract OCPs from soil as an alternative to common Soxhlet and shake flask extraction.

Soxtec extraction, based on Soxhlet system, is a two step extraction procedure, involving a boiling and rinsing step, which drastically reduces the total time of extraction. However, reconcentration and clean-up steps are also required for both ultrasonic and soxtec extraction techniques (Pastor et al., 1997; Popp et al., 1997).

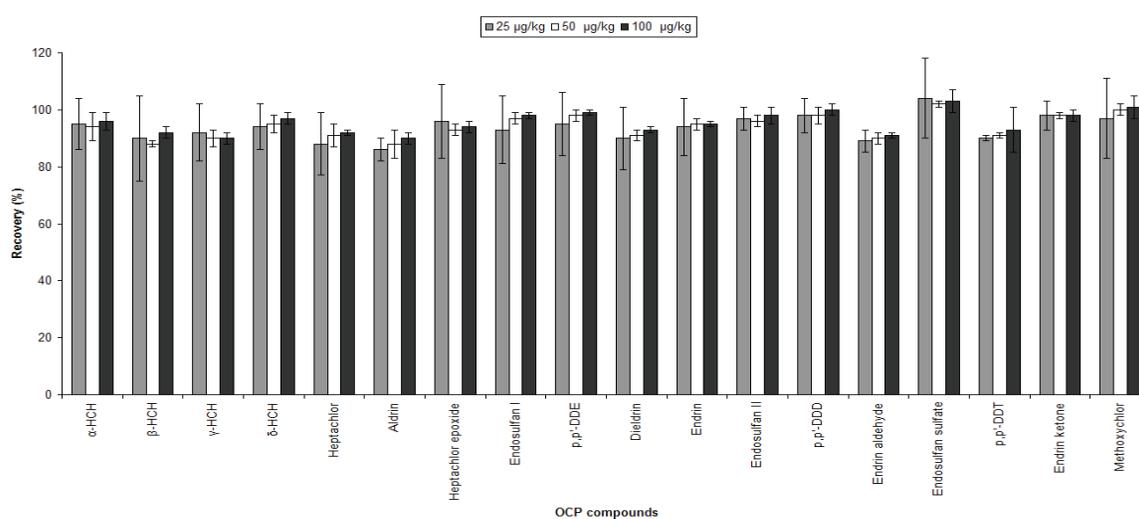


Fig. 4. Recoveries of OCPs from spiked soil with three fortification levels using miniaturised ultrasonic extraction method [ $n=5$ ]. (Extraction conditions; extraction solvent: acetone/petroleum ether (1/1, v/v), soil sample amount: 0.5 g, extraction solvent volume: 5 mL, number of extraction step: 3, extraction time: 5 minutes, temperature: 25 °C)

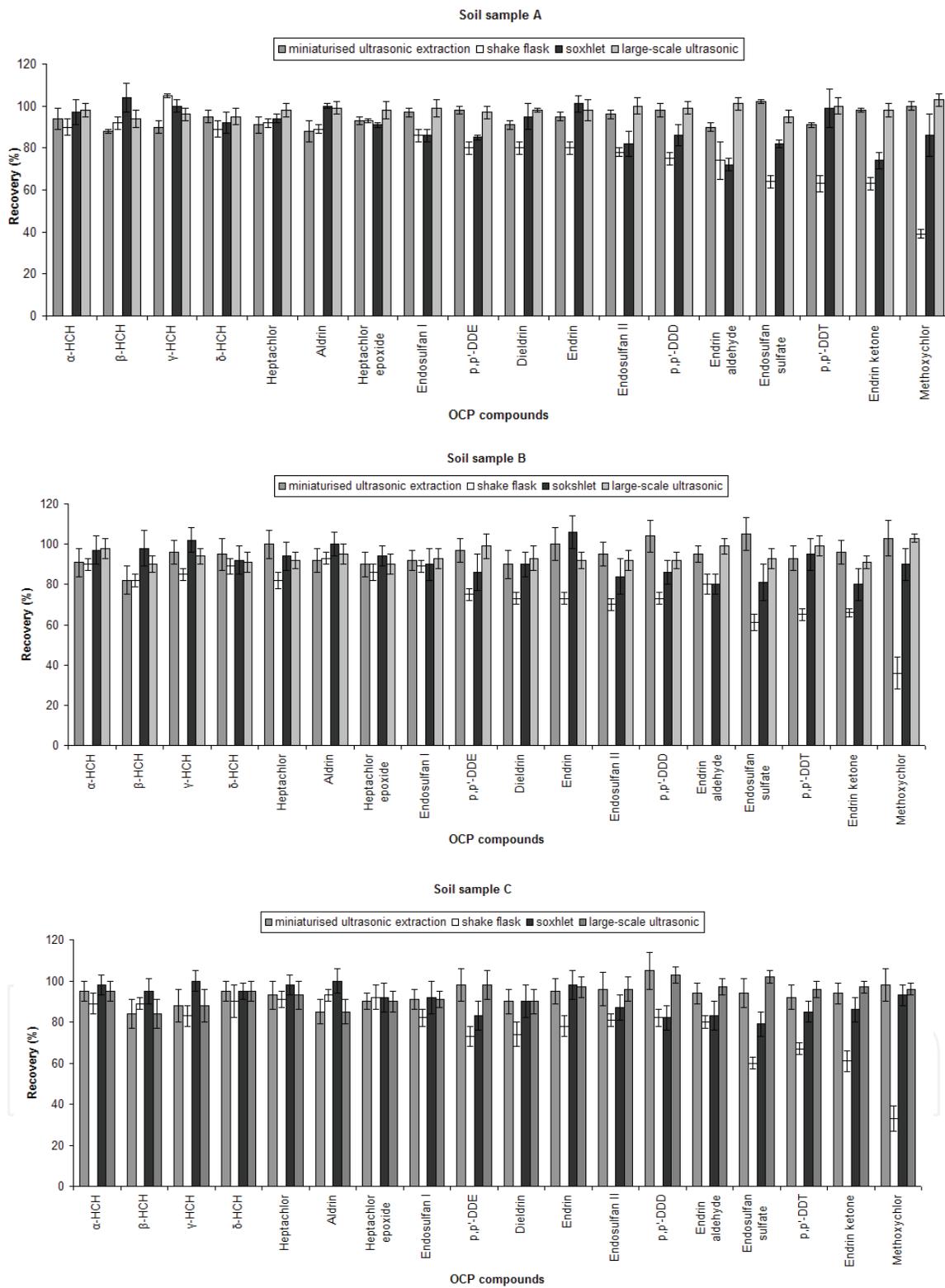


Fig. 5. Comparison of extraction efficiency of the miniaturised ultrasonic method with soxhlet, shake flask and large-scale ultrasonic extraction for OCPs in fortified real soil samples (fortification concentration for each compound:  $50 \mu\text{g kg}^{-1}$ ), [ $n=5$ ].

Apart from these methods, three more recent techniques from literature, including supercritical fluid extraction (SFE) (Sun & Lee, 2003), microwave-assisted extraction (MAE) (Eskilsson and Björklund, 2000) and accelerated solvent extraction (ASE) (Björklund et al., 2000), were also compared with for the extraction of OCPs from soil. The main key to shorter extraction times and reduced solvent consumption with these techniques is the possibility of working at elevated temperatures above the boiling point of the solvent. Thereby the extraction process is facilitated due to increased analyte desorption and diffusion from the solid matrix. SFE and ASE techniques need much lower volumes of organic solvents than other extraction techniques. Except for SFE technique, reconcentration and clean-up steps have to be performed for MAE and ASE techniques (Berset et al., 1999). Obviously the contamination risk for those extraction techniques which require reconcentration and clean-up steps are higher than that of SFE. On the other hand method development time and costs for SFE are quite high as well as for ASE (Berset et al., 1999). Compared to the conventional soxhlet and shake flask extraction techniques, the miniaturised ultrasonic solvent extraction in this study has many advantages including minimal solvent use, short extraction and preconcentration time, low cost, simplicity and ease of use. In addition, this method is cheaper and easier than MAE, ASE and SFE techniques.

## 5. Conclusion

This chapter has outlined the successful development and application of miniaturised ultrasonic extraction procedure for the determination of OCPs in water and soil samples by using GC/ $\mu$ -ECD. Analyses of real samples showed that sample matrices had no adverse effect on the efficiency of ultrasonic extraction procedure. As a consequence, the proposed miniaturised ultrasonic extraction method is precise, reproducible and rapid and easy for the analyses of OCPs in water and soil samples. It also requires only small volumes of extraction solvent and sample materials. In addition, the miniaturised ultrasonic extraction method has been demonstrated to be viable, rapid and easy to use for the qualitative and quantitative analysis of OCPs in different water and soil samples. Additionally, the miniaturised method uses less solvent than traditional approaches (i.e., liquid-liquid, solid phase, shake flask, soxhlet, large-scale ultrasonic extraction), reducing the costs associated with solvent purchase and waste disposal. The proposed method will reduce laboratory expenses without substantial new equipment and without compromising accuracy and precision. Furthermore, it is cheaper and easier than LLE, SPE, SPME, MAE, ASE and SFE techniques and it can be concluded that most commercial laboratories can efficiently use the proposed method for the extraction of OCPs from water and soil.

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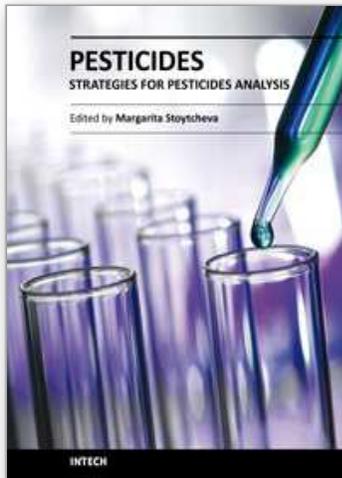
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This book provides recent information on various analytical procedures and techniques, representing strategies for reliability, specificity, selectivity and sensitivity improvements in pesticides analysis. The volume covers three main topics: current trends in sample preparation, selective and sensitive chromatographic detection and determination of pesticide residues in food and environmental samples, and the application of biological (immunoassays-and biosensors-based) methods in pesticides analysis as an alternative to the chromatographic methods for "in situ" and "on line" pesticides quantification. Intended as electronic edition, providing immediate "open access" to its content, the book is easy to follow and will be of interest to professionals involved in pesticides analysis.

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