COMPARISON OF SOXHLET EXTRACTION, MICROWAVE-ASSISTED EXTRACTION AND ULTRASONIC EXTRACTION FOR THE DETERMINATION OF PCBS CONGENERS IN SPIKED SOILS BY TRANSFORMER OIL (ASKAREL)

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ABSTRACT

In this work, we compare the extraction effectiveness of three methods commonly applied for the determination of polychlorinated biphenyls (PCBs) in the spiked soil by transformer oil (Askarel oil). The techniques included are the Soxhlet extraction (SE), the Ultrasonic extraction (UE), and the Microwave-assisted extraction (MAE). Also a comparison of organic extracting solvents was performed in this study. The extraction conditions were not optimized for these techniques; we note that the choices of extraction parameters were based on the experience from pervious successful investigation published by a number of research groups worldwide. This study focused on the variation of the extraction quantities for each PCB congener (29 PCBs) with different extraction methods. The chromatographic analysis results obtained have showed that the mixture (n-hexane-acetone, v/v) can give the highest recoveries when compared to other solvents. The comparison made between the MAE, UE and SE methods has showed that MAE is a suitable alternative to SE for the analysis of PCBs in soils, but UE did not give a good recovery in the present work.

KEYWORDS: *Soxhlet extraction, Microwave-assisted extraction, Ultrasonic extraction, Polychlorinated biphenyls, Soil, GC-ECD.*

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) are listed along with 11 other organic compounds by Stockholm convention as the persistent organic pollutants that could threaten the environment matrices (soil, plante, air, water) and human health [1-3].

PCBs are a class of synthetic organic compounds with general chemical formula $C_{12}H_{10-n}Cl_n$ with n ranging between 1 and 10; as a consequence 209 different configurations or congeners are possible. Each chlorinated biphenyl (CB) congener is named according to the position of chlorine number from 1 to 209 (Ballschmiter and zell) [1-4].

The PCBs were primarily used as a transformer insulating oil. Until 1979, its usage was prohibited by united states congress, its commercial production had been started from 1930: about 1,3 million tons were been produced worldwide as industrial chemical for various applications such as dielectric fluids in electrical transformers (e.g. oil transformer: Askarel), capacitors, hydraulic fluids, lubricating and cutting oils, additives in sealant, plastics, paints, copying paper, adhesives and casting agents [5.6].

Interest in the toxicological effect of PCBs has been focused on a small group of planar congener, which are referred to as coplanar PCBs. Coplanar PCBs (or non-orhto PCBs) have a close structural similarity to that of the tetrachlorodibenzo-p-dioxins, because toxicity correlates strongly with such structures, the toxicity of PCB mixtures may result from the presence of such compounds (called PCB dioxin-like) [4,7,8].

Because of their high thermodynamic stability, all degradation mechanisms are difficult, and environmental and metabolic degradation is generally very slow [5]. Their thermal stability and resistance to degradation contributed to their commercial usefulness, but also to their long-term environmental effects. Similar to dioxins, PCBs have accumulated in soils and sediments. Globally, approximately 21,000 tons of PCBs have been discharged into the surface soils estimated by (Meijer et al) [9], there are still a countless number of electric transformers and capacitor around the cities filled *ASKAREL*, a mineral oil containing PCBs [10,11]. In Algeria, PCBs were widely used mainly as dielectric fluids in the past 50 years and some still remain in use or in storage (6699 apparatus containing over 3443 tons of Askarel oil have been inventoried) [6].

For this the Soil is an important reservoir for PCBs and plays an important role in the global cycling and food chain transfer of PCBs[12-14]. Although PCBs are subject to redistribution and transformation processes once into the soil, they can still accumulate in horizons rich in organic matter [1,6,14-17]. However, for the determination of PCBs in environmental solid, it is imperative to develop extraction techniques for the analysis of PCBs in the soil, in order to minimize waste solvents and to shorten the analytical procedures and the time.

The purpose of the present study was to determine and to compare the recoveries concentrations of 29 congeners CBs in spiked soil, using three different extraction methods (conventional Soxhlet Extraction (SE), Ultrasonic Extraction (UE) and microwave-assisted extraction (MAE)); the extraction condition have not been optimized individually for each extraction method, but chosen from a comprehensive reference list which covers many of the most important articles published on extraction PCBs from various matrices [2,4,12,14,16-19,23-26,30-39], and as well as to take a consideration the recoveries of PCBs from soil , other comparators are necessary and this include capital and running costs, organic solvent usage and operator skill.

Askarel oil is major source of contaminate soil by PCBs in Algeria, for this the mean objective of the current work was test the efficiency of microwave-assisted extraction (with an adapted domestic microwave oven) for the determination of the 29 congeners PCBs in spiked soil by Askarel oil . To the best of authors knowledge, this study may be the first report describing comparison between MAE methods and SE, UE for determination 29 PCBs congeners in contaminated soil by transformer oil (Askarel). This method represents fast, low-solvent consumption and low cost, MAE can be will alternative to SE method for extraction PCBs from contaminated soils and sediments in laboratories of countries under development (Algeria).

II. RELATED WORKS

The conventional and classical method well-known for the extraction of PCBs from environmental matrices is the Soxhlet extraction (SE) [18-21]. But the SE method has two main disadvantages: the first one, large volumes of organic solvent are required; the second is that, to achieve an exhaustive extraction can require several hours to days. in recent years other novels extraction techniques have been developed for extraction PCBs such as Ultrasonic extraction (UE) [22-25], supercritical fluid extraction (SFE) [18-21,25,26], and Accelerated solvent extraction (ASE) [19-21,26-30], in order the significantly decreased the extraction time and solvent consumption, but their costs is very expensive.

The microwave assisted extraction method (MAE) was first reported by (Ganzler et al) for extracted of organic pollutants from solid matrices and subsequently has been applied in many studies [19, 30-39].

Many studies considered the SE method as reference and benchmark for the evaluation of many other extraction methods [19, 30-32]. By the same way, in the present paper, this method (SE) is taken as reference for the evaluation of MAE and UE methods

III. ORGANIZATION OF THE MANUSCRIPT

Experimetal - This section explains the experimental procedure used for the determination of PCBs in a soil sample. The first step is the preparation of spiked soil samples, reagents and chemicals. The next steps are as follows: extraction and cleanup, details of each extraction methods, and finally the description of the chromatographic apparatus performed for quantifying the PCBs.

Results and Discussion: This section presents the results of the PCBs concentrations given by three extraction methods. It discusses also the effect of the extracting solvent for each method. Finally, a comparison study between the three methods is made.

Conclusion: It recapitulates all the summary of the experiment performed along with the brief of what we achieved in results.

IV. EXPERIMENTAL

4.1 Soil samples and spiked sample preparation

Surface soil samples were collected (30–40 cm depth) from an agricultural site in southern Algiers. After discarding any foreign object such as sticks, leaves and rocks, the uncontamined soil was air dried at room temperature (35°C) to constant weight for 24 h, sieved to <1 mm, homogenized (3h, 220rpm) and finally frozen (-20°C) inside closed amber flask until further analysis [22,40].

Uncontamined Soil samples (1kg) was spiked with a mixture of PCBs (transformer oil) such that the final spiked concentration was 1µg /g of target analytes, then homogenized , all spiked soils were stored at -20°C in a freezer until extraction [19,40].

4.2 Reagents and chemicals

Aroclor 1260, Aroclor 1248, Aroclor 1254, Aroclor 1242, Aroclor Mix 1 containing a total of four congeners (Aroclor 1016, Aroclor 1260, Aroclor 1232, Aroclor 1248[1:1:1:1]) and Dichlobenil were commercially available with a purity of 99% (Supelco). The sorbents Florisil (60-100 mesh) and anhydrous sodium sulphate were purchased from Panreac (para analysis, Barcelona Spain) and all solvents (acetone, n-hexane and dichloromethane (DCM)) were Chromasol for HPLC grade and purchased from Sigma–Aldrich (Laborchemilkalian GmbH).

4.3 Extraction and cleanup

All spiked soil samples (10g mixed with anhydrous sodium sulphate and copper powder) were subjected to MAE, UE and SE.

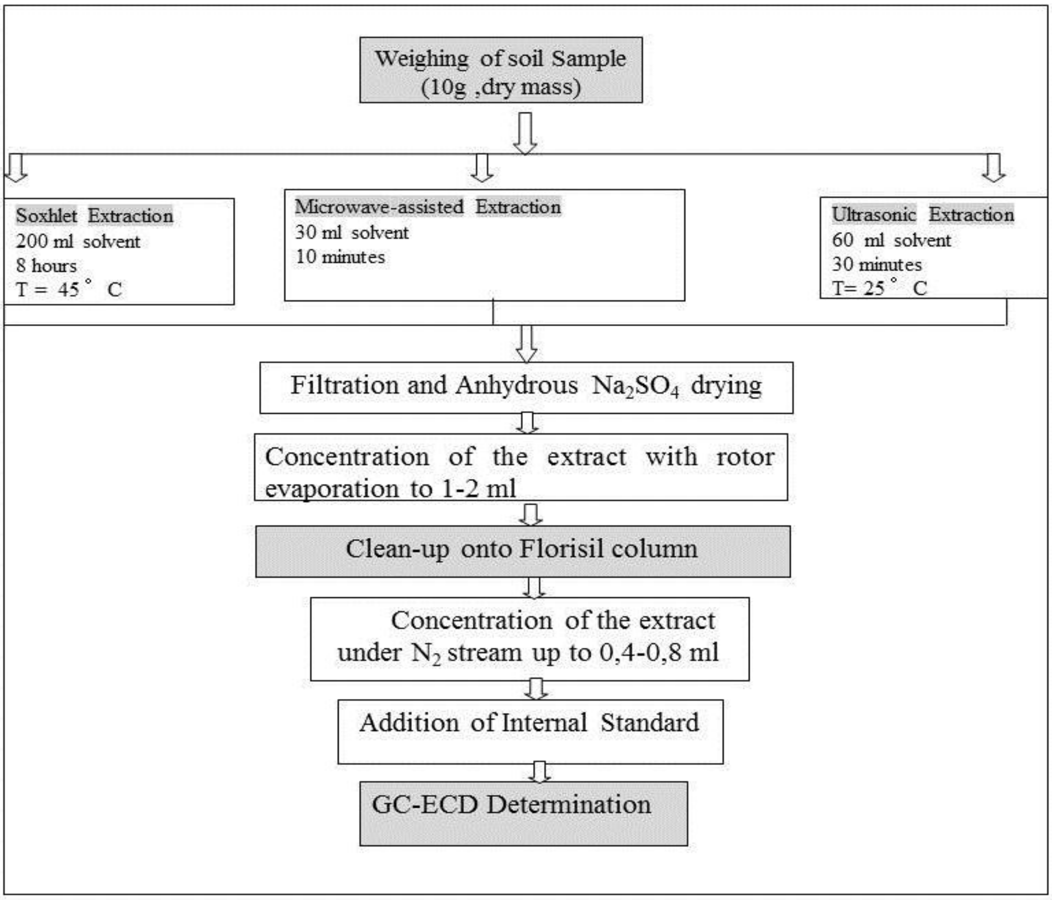


Figure 1. Experimental procedure for the determination of PCB in soil samples.

The extracts were filtered and concentrated to a volume of 1 – 2ml by rotary vaporation under reduced pressure at 50°C, then eluted through florisil column (Florisil, 60-100 mesh size, activated for 2 hours at 500°C, deactivated with 4% of demineralised water) with hexane [41,42]. Sample extraction and clean-up procedures followed previously established method with some modifications (Figure 1).

Three famous extractions solvents applied in many previous studies for extract PCBs from solid matrixes: n-hexane/acetone (1:1, v/v), n-hexane/ DCM (1:1, v/v), and DCM, was employed in this study to extract PCBs from spiked soil.

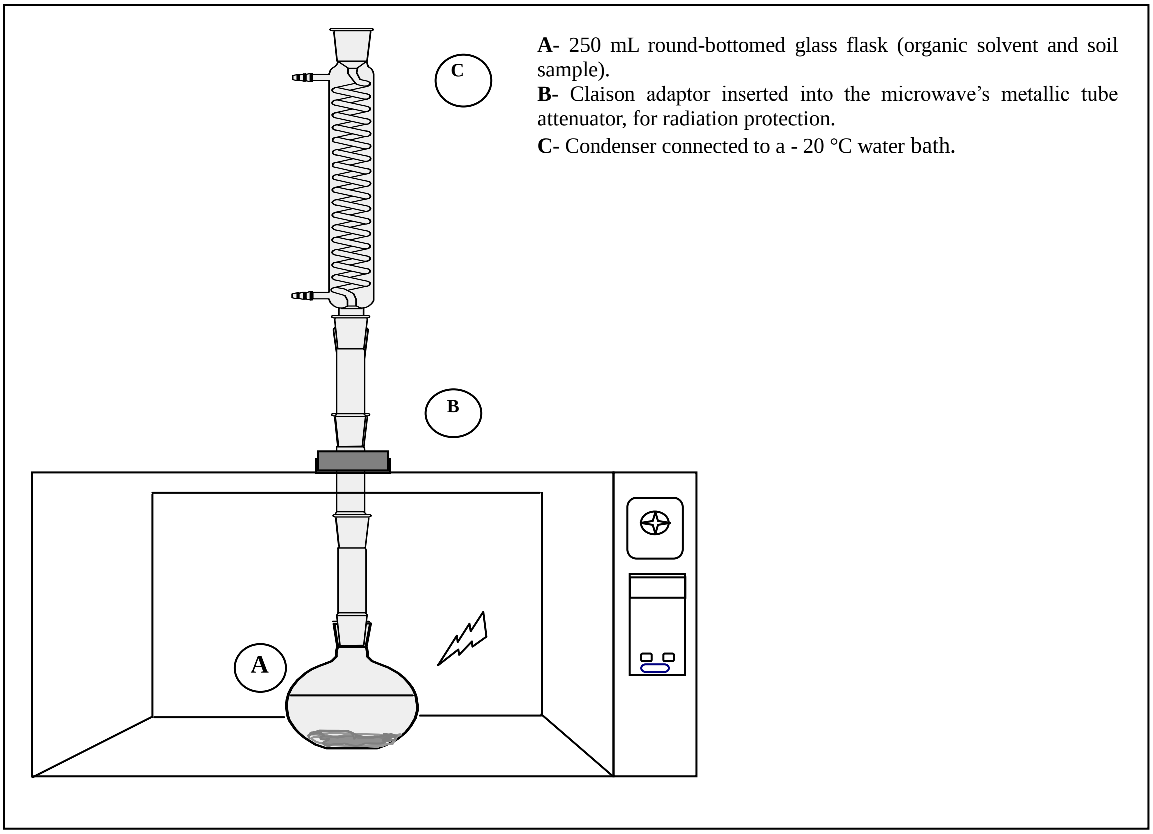
4.3.1 Soxhlet extraction

SE was performed using about 10.0g spiked soil mixed with 2g anhydrous sodium sulphate (Na_2SO_4), This mixture was placed in a pre-washed cellulose SE thimble and extracted with 250mL of the chosen solvent (n-hexane/acetone (1:1, v/v), n-hexane/DCM (1:1, v/v) or DCM) for 8h at a rate of 7-8 cycles/h, in a prewashed glass fibre thimble. Extracts were concentrated in rotavapor system (Heidolph, LABORATQ 4001,Germany) then went through the clean-up procedure described below.

4.3.2 Microwave assisted extraction

Microwave assisted extraction (MAE) (Figure 2) was performed with a modified domestic oven (650 W, 2450 MHz) M1933N SAMSUNG, Corea) , based on the work by Nuno Ratola et al[31], Herbert et al [43] and Ganzler et al[44].

The spiked soil sample 10g and 2g Na_2SO_4, were quantitatively weighed and transferred into the extraction flask. 30 mL solvent (n-hexane/acetone (1:1, v/v), n-hexane/DCM (1:1, v/v), DCM) was added and the extraction was performed for 10min at 520 W. (A household microwave oven equipped with a magnetron of 2450 MHz (maximum power, 650 W), and a thermostated water batch were also used).



A- 250 mL round-bottomed glass flask (organic solvent and soil sample).

B- Claison adaptor inserted into the microwave's metallic tube attenuator, for radiation protection.

C- Condenser connected to a - 20 °C water bath.

Figure .2. Scheme of the microwave assisted extraction (MAE) apparatus used in this work (adapted by Herbert et al and Ganzler et al).

4.3.3 Ultrasonic extraction

Same amount of weighed sample as in SE was introduced in a vessel mixed with the chosen solvent (n-hexane/acetone (1:1, v/v), n-hexane/DCM (1:1, v/v) or DCM). The container was placed in an ultrasonic bath (Fisher Scietific, Made France, Frequency of 60KHz, nominal power 90W and 24 cm×14 cm×10 cm internal dimensions water bath) for 30min. The extracts were filtrated and washed.

4.3.4 Clean-up procedure

Sample clean-up procedure followed our previously established method with some modifications [41-42].

After each sample extraction procedure, organic extracts are evaporated to dryness and dissolved in 1-2 ml hexane. The elution was done with 50 ml n-hexane through florisil column prepared according to slurry packing technique (1cm x 25 cm glass column contained 5g Florisil conditioning for 4 h at 250°C then deactivated with 5% of water) and rinsed with 50 ml n-hexane before use. The obtained fraction was reduced to 800µl then 100µl of dichlorbinyl (10ng/µl) was added into the solution before gas chromatography analysis.

4.4 Instrumental analysis

The determination of PCBs were analyzed using GC-ECD (*Perkin Elmer instruments Clarus 500)* equipped with a *CP Sil 5CB* capillary column *(60 m*0,25mm*0.25 µm, Supelco),*and the software : *Total Chrom version 5.1* , and the detector of the radioactive source (ECD- Ni^{63}) at a constant flow rate 1 ml /min , N_2 as a carrier gas. The initial column temperature was maintained at 75 °C during 2 min, and then increased to 150°C at the rate 15 °C /min, and finally to to 300°C at 1.5°C /min. Injector and detector temperatures were 310 °C and 300 °C, respectively. Nitrogen used as carrier and make-up-gase. A 1 µl solution was injected in splitless mode.

The quantification of PCBs was performed using external standard calibration (Aroclor *1260*), and the average response factor was generated from five point calibration a range between (0.1 and 1 µg/mL). Integration and calculation were accomplished using (*Total Chrom version 5.1)* software. The linearity for quantification was in the range of 0.1-1 µg/ml (Arochlor *1260*); the DLs (SD x 3) of PCB congeners by GC-ECD were approximately 0.05 ng/g.

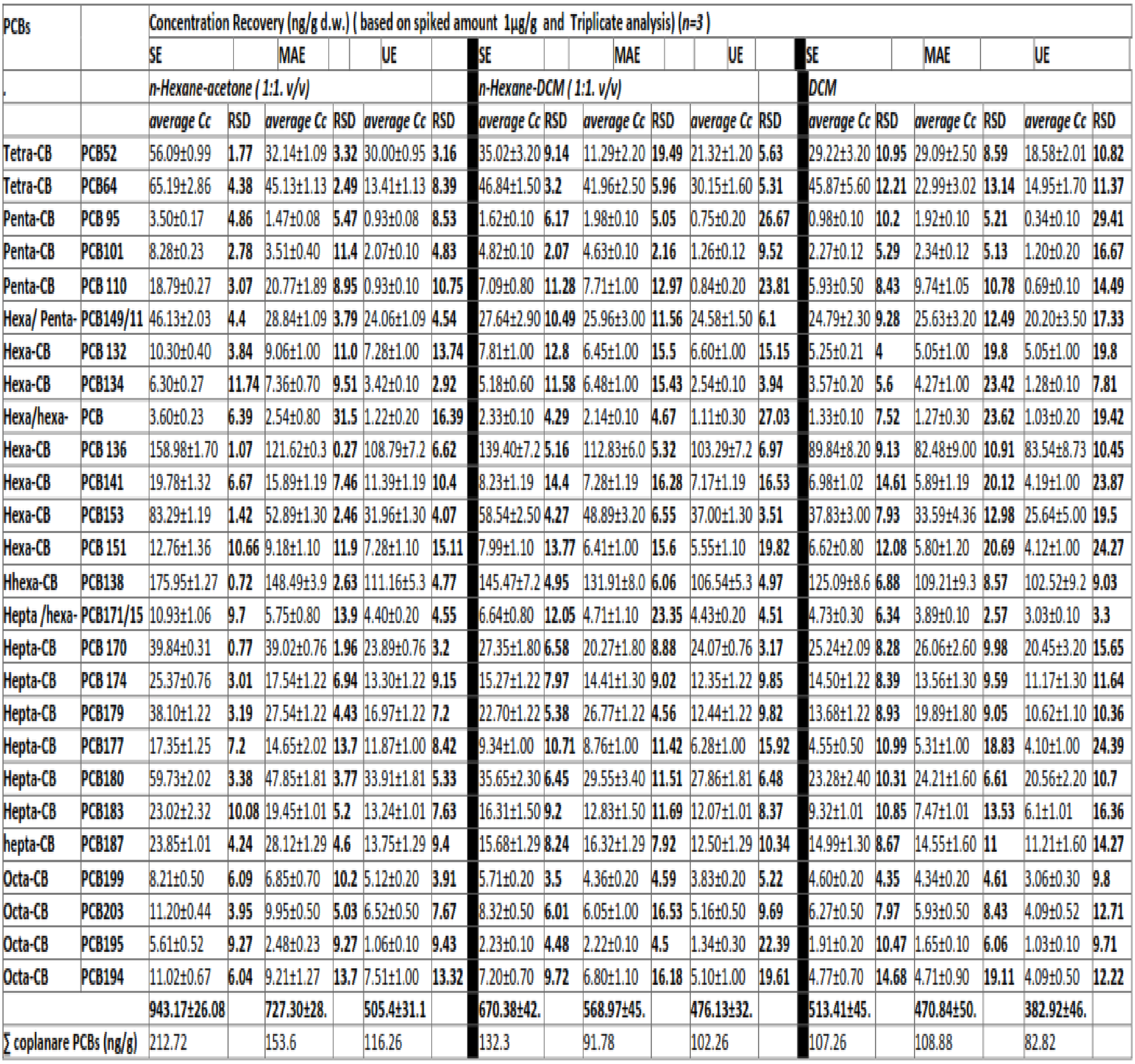
V. RESULTS AND DISCUSSION

The particular PCB congeners, as well as the soil type, amount of organic matter and moisture affect how readily and how strongly the PCBs adsorbed into soils and sediments. Also the performance of an analytical methodology can be enhanced if a selective extraction procedure is employed that directly decreases or eliminates interfering substance in the extract and gives high yield [4]. For this purpose, a comparison between the three methods has been investigated in this paper. We note that each extraction has been performed three times.

Table 1 presents the concentration of 29 PCBs congeners *(2Tetra-CBs, 4Penta-CBs, 11Hexa-CBs, 8 Hepta-CBs and 4 Octa-CBs)*. From there, there are 8 PCBs coplanar which were extracted from spiked soil matrices by using the three methods. We note that we have tested three different extracting solvents for each method.

The total concentrations of PCBs congeners (Σ PCBs) obtained by the SE, MAE and UE methods were *(943.17- 513.41 ng/g)*, *(*727.30 - 470.84 *ng/g)*, and *(505.4 – 382.92 ng/g)*, respectively. The conventional method SE has given a high recovery for all PCBs congeners. The results of concentration for individual congeners have showed the highest recoveries for *PCB 134, PCB 153* and *PCB138* in all extracted samples.

Table 1. The average concentration of PCBs congeners and thiers relative standard deviation (RSD) in spiked soil samples (triplicate analysis *n=3*) using three different extraction methods: Soxhlet (SE). Microwave assisted (MAE) and Ultrasonication extractions (UE). and using three different solvents extractions. b) target PCBs & coeluting peaks. Values (average mean ± SD) are average of three extracts of each soil sample analysed individually in triplicate (n = 1x3 x3)



PCBs		Concentration Recovery (ng/g d.w.) (based on spiked amount 1µg/g and Triplicate analysis) (*n=3*)																	
		SE		MAE		UE		SE		MAE		UE		SE		MAE		UE	
.		*n-Hexane-acetone (1:1. v/v)*						*n-Hexane-DCM (1:1. v/v)*						*DCM*					
		average Cc	RSD	*average Cc*	RSD	*average Cc*	RSD	*average Cc*	RSD	*average Cc*	RSD	*average Cc*	RSD	*average Cc*	RSD	*average Cc*	RSD	*average Cc*	RSD
Tetra-CB	PCB52	56.09±0.99	1.77	32.14±1.09	3.32	30.00±0.95	3.16	35.02±3.20	9.14	11.29±2.20	19.49	21.32±1.20	5.63	29.22±3.20	10.95	29.09±2.50	8.59	18.58±2.01	10.82
Tetra-CB	PCB64	65.19±2.86	4.38	45.13±1.13	2.49	13.41±1.13	8.39	46.84±1.50	3.2	41.96±2.50	5.96	30.15±1.60	5.31	45.87±5.60	12.21	22.99±3.02	13.14	14.95±1.70	11.37
Penta-CB	PCB 95	3.50±0.17	4.86	1.47±0.08	5.47	0.93±0.08	8.53	1.62±0.10	6.17	1.98±0.10	5.05	0.75±0.20	26.67	0.98±0.10	10.2	1.92±0.10	5.21	0.34±0.10	29.41
Penta-CB	PCB101	8.28±0.23	2.78	3.51±0.40	11.4	2.07±0.10	4.83	4.82±0.10	2.07	4.63±0.10	2.16	1.26±0.12	9.52	2.27±0.12	5.29	2.34±0.12	5.13	1.20±0.20	16.67
Penta-CB	PCB 110	18.79±0.27	3.07	20.77±1.89	8.95	0.93±0.10	10.75	7.09±0.80	11.28	7.71±1.00	12.97	0.84±0.20	23.81	5.93±0.50	8.43	9.74±1.05	10.78	0.69±0.10	14.49
Hexa/ Penta-	PCB149/11	46.13±2.03	4.4	28.84±1.09	3.79	24.06±1.09	4.54	27.64±2.90	10.49	25.96±3.00	11.56	24.58±1.50	6.1	24.79±2.30	9.28	25.63±3.20	12.49	20.20±3.50	17.33
Hexa-CB	PCB 132	10.30±0.40	3.84	9.06±1.00	11.0	7.28±1.00	13.74	7.81±1.00	12.8	6.45±1.00	15.5	6.60±1.00	15.15	5.25±0.21	4	5.05±1.00	19.8	5.05±1.00	19.8
Hexa-CB	PCB134	6.30±0.27	11.74	7.36±0.70	9.51	3.42±0.10	2.92	5.18±0.60	11.58	6.48±1.00	15.43	2.54±0.10	3.94	3.57±0.20	5.6	4.27±1.00	23.42	1.28±0.10	7.81
Hexa/hexa-	PCB	3.60±0.23	6.39	2.54±0.80	31.5	1.22±0.20	16.39	2.33±0.10	4.29	2.14±0.10	4.67	1.11±0.30	27.03	1.33±0.10	7.52	1.27±0.30	23.62	1.03±0.20	19.42
Hexa-CB	PCB 136	158.98±1.70	1.07	121.62±0.3	0.27	108.79±7.2	6.62	139.40±7.2	5.16	112.83±6.0	5.32	103.29±7.2	6.97	89.84±8.20	9.13	82.48±9.00	10.91	83.54±8.73	10.45
Hexa-CB	PCB141	19.78±1.32	6.67	15.89±1.19	7.46	11.39±1.19	10.4	8.23±1.19	14.4	7.28±1.19	16.28	7.17±1.19	16.53	6.98±1.02	14.61	5.89±1.19	20.12	4.19±1.00	23.87
Hexa-CB	PCB153	83.29±1.19	1.42	52.89±1.30	2.46	31.96±1.30	4.07	58.54±2.50	4.27	48.89±3.20	6.55	37.00±1.30	3.51	37.83±3.00	7.93	33.59±4.36	12.98	25.64±5.00	19.5
Hexa-CB	PCB 151	12.76±1.36	10.66	9.18±1.10	11.9	7.28±1.10	15.11	7.99±1.10	13.77	6.41±1.00	15.6	5.55±1.10	19.82	6.62±0.80	12.08	5.80±1.20	20.69	4.12±1.00	24.27
Hhexa-CB	PCB138	175.95±1.27	0.72	148.49±3.9	2.63	111.16±5.3	4.77	145.47±7.2	4.95	131.91±8.0	6.06	106.54±5.3	4.97	125.09±8.6	6.88	109.21±9.3	8.57	102.52±9.2	9.03
Hepta /hexa-	PCB171/15	10.93±1.06	9.7	5.75±0.80	13.9	4.40±0.20	4.55	6.64±0.80	12.05	4.71±1.10	23.35	4.43±0.20	4.51	4.73±0.30	6.34	3.89±0.10	2.57	3.03±0.10	3.3
Hepta-CB	PCB 170	39.84±0.31	0.77	39.02±0.76	1.96	23.89±0.76	3.2	27.35±1.80	6.58	20.27±1.80	8.88	24.07±0.76	3.17	25.24±2.09	8.28	26.06±2.60	9.98	20.45±3.20	15.65
Hepta-CB	PCB 174	25.37±0.76	3.01	17.54±1.22	6.94	13.30±1.22	9.15	15.27±1.22	7.97	14.41±1.30	9.02	12.35±1.22	9.85	14.50±1.22	8.39	13.56±1.30	9.59	11.17±1.30	11.64
Hepta-CB	PCB179	38.10±1.22	3.19	27.54±1.22	4.43	16.97±1.22	7.2	22.70±1.22	5.38	26.77±1.22	4.56	12.44±1.22	9.82	13.68±1.22	8.93	19.89±1.80	9.05	10.62±1.10	10.36
Hepta-CB	PCB177	17.35±1.25	7.2	14.65±2.02	13.7	11.87±1.00	8.42	9.34±1.00	10.71	8.76±1.00	11.42	6.28±1.00	15.92	4.55±0.50	10.99	5.31±1.00	18.83	4.10±1.00	24.39
Hepta-CB	PCB180	59.73±2.02	3.38	47.85±1.81	3.77	33.91±1.81	5.33	35.65±2.30	6.45	29.55±3.40	11.51	27.86±1.81	6.48	23.28±2.40	10.31	24.21±1.60	6.61	20.56±2.20	10.7
Hepta-CB	PCB183	23.02±2.32	10.08	19.45±1.01	5.2	13.24±1.01	7.63	16.31±1.50	9.2	12.83±1.50	11.69	12.07±1.01	8.37	9.32±1.01	10.85	7.47±1.01	13.53	6.1±1.01	16.36
hepta-CB	PCB187	23.85±1.01	4.24	28.12±1.29	4.6	13.75±1.29	9.4	15.68±1.29	8.24	16.32±1.29	7.92	12.50±1.29	10.34	14.99±1.30	8.67	14.55±1.60	11	11.21±1.60	14.27
Octa-CB	PCB199	8.21±0.50	6.09	6.85±0.70	10.2	5.12±0.20	3.91	5.71±0.20	3.5	4.36±0.20	4.59	3.83±0.20	5.22	4.60±0.20	4.35	4.34±0.20	4.61	3.06±0.30	9.8
Octa-CB	PCB203	11.20±0.44	3.95	9.95±0.50	5.03	6.52±0.50	7.67	8.32±0.50	6.01	6.05±1.00	16.53	5.16±0.50	9.69	6.27±0.50	7.97	5.93±0.50	8.43	4.09±0.52	12.71
Octa-CB	PCB195	5.61±0.52	9.27	2.48±0.23	9.27	1.06±0.10	9.43	2.23±0.10	4.48	2.22±0.10	4.5	1.34±0.30	22.39	1.91±0.20	10.47	1.65±0.10	6.06	1.03±0.10	9.71
Octa-CB	PCB194	11.02±0.67	6.04	9.21±1.27	13.7	7.51±1.00	13.32	7.20±0.70	9.72	6.80±1.10	16.18	5.10±1.00	19.61	4.77±0.70	14.68	4.71±0.90	19.11	4.09±0.50	12.22
		943.17±26.08		727.30±28.		505.4±31.1		670.38±42.		568.97±45.		476.13±32.		513.41±45.		470.84±50.		382.92±46.	
∑ coplanare PCBs (ng/g)		212.72		153.6		116.26		132.3		91.78		102.26		107.26		108.88		82.82	

Many studies considered the SE method as a reference and a benchmark for the evaluation of many other extraction methods [19,30-32]. By the same way, in the present paper, this method (SE) is taken as a reference for the evaluation of MAE and UE methods. For this purpose, three mixture solvent are used, which were: n-hexane/acetone, n-hexane/DCM, and DCM.

By using the SE method, Figure 3 shows the results of the concentrations of 29 PCBs congeners extracted from spiked soil samples. It was found that the recoveries are higher for all 29 PCB congeners when the mixture of n-hexane/acetone was used as extracting solvent, except for case of the congener PCB134 where the n-hexane/DCM has given the good recovery.

We conclude that SE using (n-hexane/acetone) like extracting solvent is suitable as a reference technique for evaluated other methods (MEA and UE) to extract PCBs compounds from soil.,

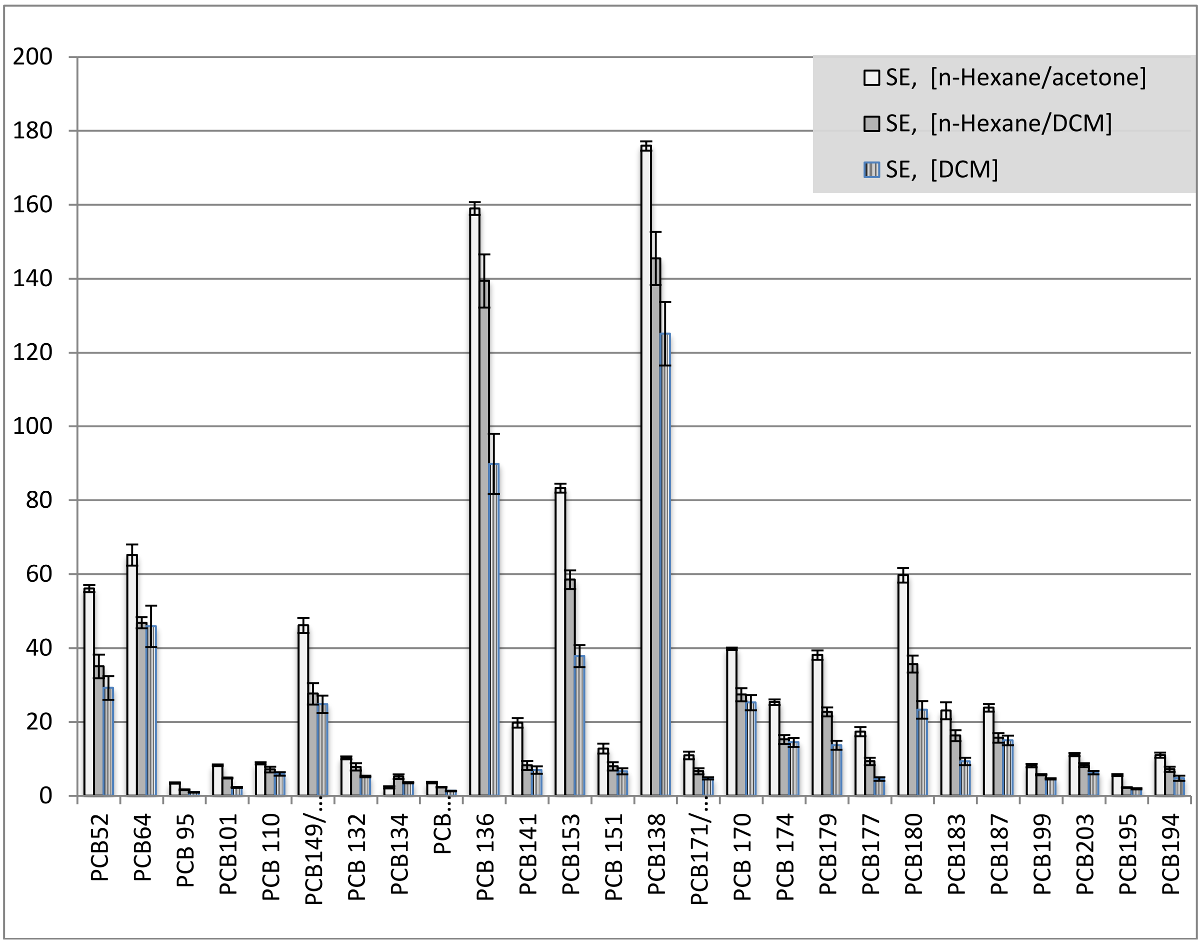


Figure 3. Concentration of PCBs congeners extracted from spiked soil by *soxhlet extraction* using three extracting solvents (*n-hexane /acetone (1:1) , DCM/n-hexane (1 :1) and DCM*) .

5.1 Effect of the extraction solvent

The extraction solvent, temperature, time, moisture content of sample, power, cycles of extraction would affect the extraction efficiency of analytical methods for determination PCBs. In this study, two effects of relatively important factors (extraction method and solvent choice), were investigated. The effects of extracting solvent on the PCBs analysis in spiked soil are presented on figures 3, 4 and 5.

Generally, the mixture of n-hexane and acetone (1:1 volume) which was used as a polar solvent have achieved high recoveries, the responses of the polar compounds were significantly improved (Figure 3 and 4). This is due to the addition of acetone to hexane which can improve the polarity of the solvent and consequently can reduce the adsorption of polar compounds onto soil. These results agree well with the finding of Kiguchi et al. [46] which indicate that the mixture (n-hexane/ acetone) solvent extracting yielded better recoveries of PCBs than when used the solvent (acetone only), and indicate also that the polar solvent extracting acetone achieved better recoveries of PCBs than a solvent extracting no polar (hexane only).

Our results indicate that dichloromethane (halogenated solvent) was rejected in favour of (hexane-acetone), this in accordance with the findings reported by Floch et al. [47]. An increase in the extraction yield for PCBs by the addition of DCM to hexane (non-polar solvent), generally for efficiency extraction method of PCBs need to be extracted by mixture of more polar organic solvents.

Also relative PCBs polarity is generally inversely proportional to the degree of chlorination. However, solvents with low polarity give low PCBs recoveries, the case of hexane in extracting PCBs.

5.2 Comparison of Soxhlet extraction (SE), MAE and UE reproducibility

Table 1 presents the analytical relative standard deviation (R.S.D.) values of 29 PCBs extracted from spiked soil matrices by the methods of SE, MAE and EU. The comparison of the precision of the procedures, by analysis of the R.S.D. of the 29 PCBs congeners extracted, showed no significant differences, and all the obtained R.S.D. values were lower than 30%, which was in the range of standard values from U.S. EPA (Recovery: 70-130%, RSD: <30%). the result of R.S.D. of SE, MAE, and UE obtained, is respectively, with n-hexane/acetone *(<12%,<14%,<16%)*, with n-hexane/DCM *(<14%,<24%,<24%)* and with DCM *(<15%,<24%,<30%)*, this result is similarly to other studies [2,14,16,23,27,30,37,38].

5.3 Comparison of Soxhlet extraction , MAE and UE recoveries (for 29 PCBs congeners)

Comparisons of recoveries obtained with both methods (MAE and UE) versus reference Soxhlet method for extracted each PCB congeners, using as solvents extractions (n-hexane/acetone, n-hexane/DCM and DCM), are presented in Figure 4.

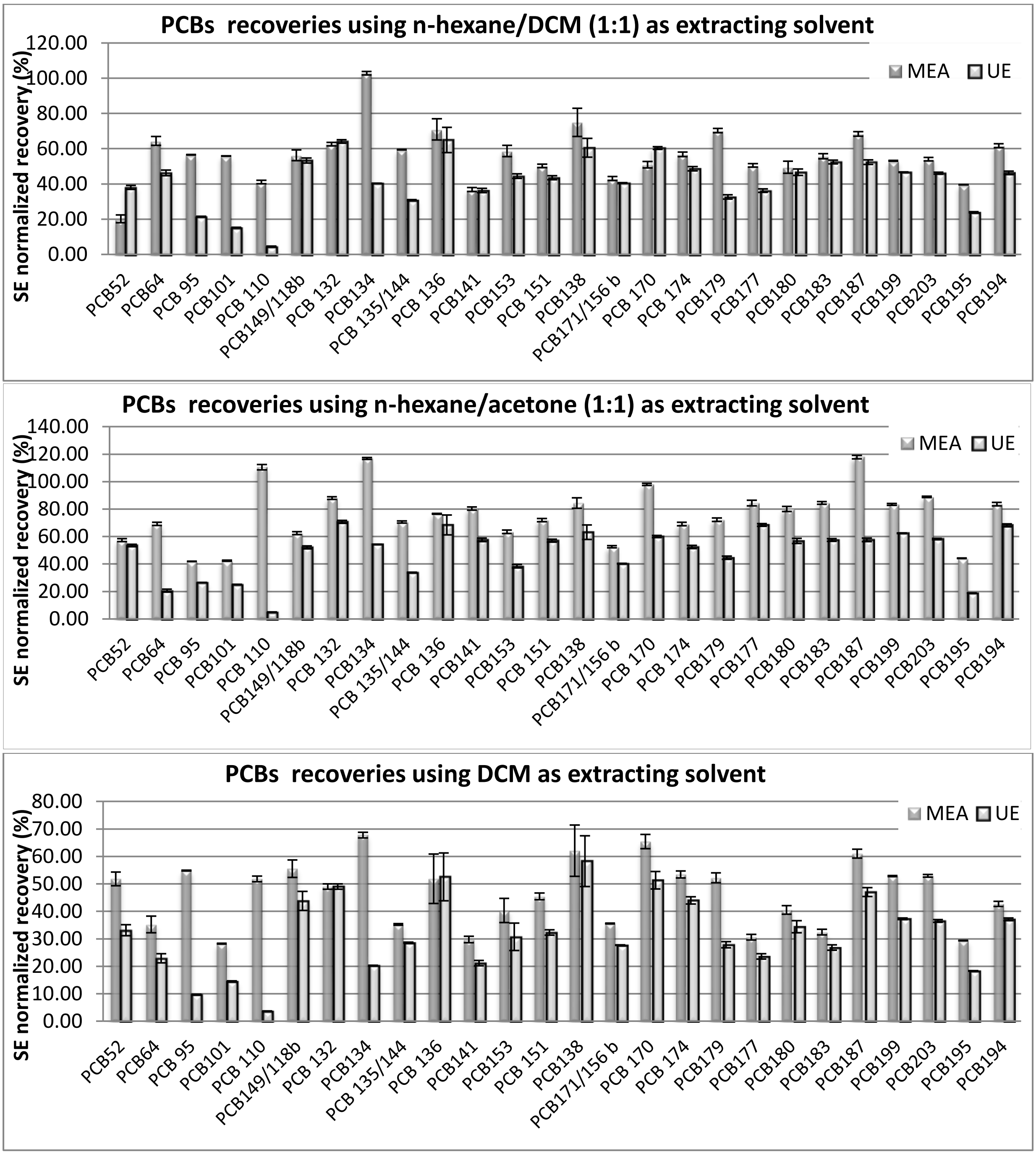


Figure 4. The recoveries %of 29 PCB congeners in the spiked soil for MAE and UE using different extracting solvents, normalized to the Soxhlet method (n=3).

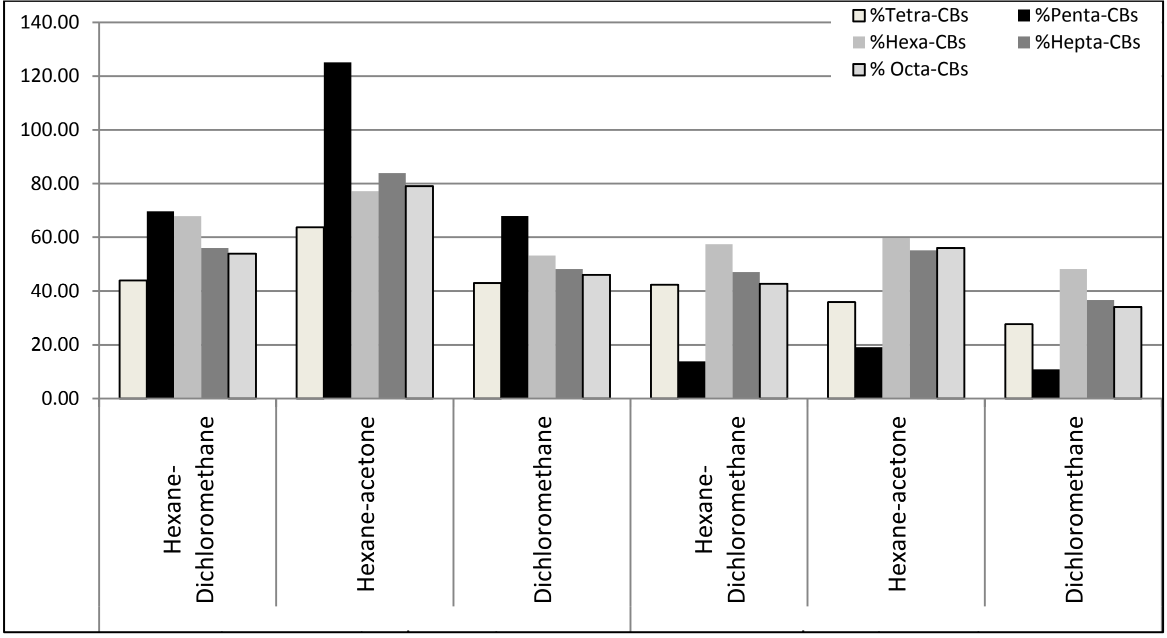


Figure 5. Recoveries of % PCB congeners (Tetra, Hexa, Octa, Penta and Hepta-CBs) in the spiked soil for MAE and UE using different extracting solvents, normalized to the Soxhlet method (n=3).

5.3.1 Microwave assisted extraction method

The extraction efficiency of MAE was observed to be nearly identical to the standard SE for most of PCBs congeners (Table 1), and this illustrates that the extraction time, power and solvent among applied are sufficient for the MAE to extract PCBs [4, 19, 29, 30]. Also, the results of MAE show a good recoveries for (*PCB 95; PCB134; PCB153; PCB179; PCB 187; PCB 183 and PCB 171/156*) than those obtained with SE when we used n-hexane/DCM (fig 4), and *(PCB 110 ; PCB 134)* when we used n-hexane/acetone.

The results presented on figures 4 and 5 show that the MAE provided high recoveries (efficiencies) and shorter extraction time that the UE and these results are in according with those given by Cai et al. [45] who interested to the determination of persistent trace organic contaminants from biota samples.

All recoveries of 29 PCBs congeners obtained with the MAE are consistently higher than those obtained with the UE, for all solvent mixture tested in this study (Figure 4). However, we can explain these results by the heat transfer in the MAE which is via the direct absorption of Microwave energy by reactants inside the pressure vessel. The energy transfer is instantaneous and the temperature of the reactants rises rapidly. The greater dielectric constant, the more thermal energy is released and more rapid is the heating for a given frequency, threshold activation temperatures for exothermic reactions are reached more quickly in microwave-heated systems [33]. This may be one reason for the high recoveries of PCBs from spiked soil in a short time.

5.3.2 Ultrasonic extraction method

For the ultrasonic extraction method (figure 4), the concentrations of PCBs congeners obtained from the extracts are consistently low for all mixtures solvents used in this study. This is maybe due to the methodology chosen in our study, which needs more optimisation. Also, for better performance and to increase the recoveries, it is necessary to use one to three extraction cycles and extraction time ranging from 30 to 12 h [29].

The recovery efficiency is an important factor when an analytical method is evaluated, in Figure 4 and 5, presents analytical recoveries of total PCBs extracted from spiked soil matrices with MAE and UE versus SE as the definition of 100% recovery. The recoveries obtained from MAE and UE were (*50.67 - 78.27 %)* and (*41.15 - 54.40 %)*, respectively.

For both extraction techniques (MAE and UE), the mixture n-hexane/acetone has given higher recoveries for PCBs. Otherwise, DCM as an extraction solvent has given low recoveries.

The comparison between the three techniques shows obvious differences: the decrease is in the following order SE > MAE > UE. The SE has much better recoveries, almost three times better than the UE.

Table 2. Comparative valuation of tested extraction techniques in present study (advantage and disadvantage parameters).

Microwave-assisted extraction (MAE)(with an adapted domestic microwave oven)	
Advantages	***Disadvantage***
Good recovery for all PCBs congeners Small amount of solvent (30 ml). Small amount of sample (10 g). Reduced handling of the samples. Shorter time of extraction (10 min). Easy to use. Inexpensive system. Good accuracy.	Single extraction Need for more optimisation
Soxhlet extraction (SE) (reference method in this work)	
Advantages	***Disadvantage***
Good recoveries. Traditional technique for certification of standard materials. Inexpensive system. Easy to handle.	Larger amount of solvent (200ml) Single extraction. Very long time of extraction (8 h). Conditioning of thimbles.
Ultrasonic extraction (UE)	
Advantages	***Disadvantage***
Easy to use Short time of extraction (30 min) Small amount of solvent (60 ml)	No good recoveries for most PCBs congeners Expensive system

VI. CONCLUSIONS

The qualitative and quantitative analysis of spiked soil samples (27 extracts) by using GC-ECD have permitted to separate and identify 29 congeners.

For all extraction methods investigated in this paper, the n-hexane/acetone (1:1, v/v) solvent was found to be the most effective mixture for the extraction of all PCBs congeners from the spiked soil.

This study has illustrated that the MAE method provides a complete extraction of all the congeners analysis (29 PCBs), also , in a comparison between the MAE and SE methods, the efficiency of the SE method can reach the yield 92.9%, however, the second one can give 72.7%. We remark that the difference is slight, therefore, the MAE method can be developed for giving better results and can be improved for being a good and fast alternative of the conventional technique (SE).

In order to enhance the performance of an analytical method, it is necessary to take into account the following parameters: the purchase cost, the solvent consumption, the overall extraction time and the ease of handling. Table 2 gives an insight on this point.

In a comparison between the SE, MAE and UE, the last two methods require less extraction time and less solvent consumption, however, they require more optimisation.

VII. FUTURE WORK

For future works, we suggest the application of the microwave extraction method (MAE) method to determine the poly chloro biphenyls (PCBs) in contaminated area. The separation and identification of PCBs atropisomeres in the environment have also received less attention from researchers until present. It seems interesting to deal with this issue.

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