

Effect of Aging Organochlorine Pesticides in Various Soil Types on Their Extractability Using Selective Pressurized Liquid Extraction

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Abstract

In this study, extractability of 13 organochlorine pesticides aged in six different soil types, was investigated. Acceptable recoveries were achieved for most of the analytes spiked into five of the soil types. No apparent correlation was perceptible between the soil characteristics and extractability of the aged analytes, signifying exhaustiveness of the extraction. However, recovery was considerably minimized (<75%) in the clay ensuring the hypothesis of study stating “extraction efficiency might be matrix dependent”. Therefore, the study demonstrates importance of optimizing extraction conditions even for those believed to be less prone to matrix effect, due to distinct properties of analyte-matrix interactions.

Keywords

Organochlorine Pesticides, Extractability, Exhaustive Extraction, Matrix Effect, Soil Characteristics, Analyte-Matrix Interactions

1. Introduction

Organochlorine pesticides (OCPs) are known to be one of the most persistent organic pollutants (POPs) in the environment. Their applications have been prohibited in the developed countries, since 1970s due to their toxicity and tendency to accumulate in living organisms. However, OCPs are frequently detected in environmental samples; mainly in the soil samples [1]. Thus, continuous monitoring of the agricultural soils has greatly attracted the attentions of most researchers and legislative bodies.

“Aged soils” are soil samples spiked with pesticides and left at room tempera-

ture for certain periods that vary from 3 days to 2 years to evaluate the capacity of pesticides to form bound residues [2] [3]. Aging of pesticides in soil often results in the entrapment of the compounds in the soil organic matter or mineral lattice. The mechanisms of binding may be via formation of covalent bonds, sorption onto soil particles, and diffusion into spatially remote points such as soil macro- and micro-pores and within the soil organic matter [4].

For most pesticides, soil organic matter and clay contents are the most important properties which influence their sorption and transformation [5]-[10]. The carbon-chlorine bond is very stable towards hydrolysis and the greater the number of chlorine substitution and/or functional groups, the greater the resistance to biological and photolytic degradation.

Extraction of the POP residues in the soil matrix usually involves the conventional solid-liquid extraction methods such as solvent shake and Soxhlet extraction (SOX) [11]. However, these methods are known to be associated with a number of drawbacks including longer extraction time, labor intensiveness, demands for large quantities of hazardous organic solvents associated with high cost of both purchases and disposal [12]. Accordingly, several new extraction techniques such as supercritical fluid extraction (SFE) [13], microwave-assisted extraction (MAE) [14], ultrasonic extraction (USE) [15] [16] [17] and pressurized liquid extraction (PLE) have been developed and applied to the extraction of OCPs from soil samples [18] [19] [20].

PLE operates at high pressures and temperatures above the boiling point of the organic solvent. The use of higher temperature increases the ability of the solvent to solubilize the analytes by disrupting the strong solute-matrix interactions. It also decreases the viscosity of liquid solvents, thus allowing better penetration of the solvent into the matrix and enhancing extraction. The elevated pressure maintains the solvents as liquid at higher temperatures. Temperature associated advantages would be precluded without the use of elevated pressures [21]. PLE allows faster extractions than classical methods and requires only small volumes of solvents. As a result, its use has been extended to the analysis of trace level contaminants including OCPs [22]. PLE and MAE are considered to be matrix independent unlike the SFE [23]. However, there are evidences in the literature that revealed the extraction efficiencies are strongly influenced by the nature of the matrix. For instance, the extraction of acidic pesticides in various types of soils revealed that increase of the organic matter contents of the soil samples and aged residues have been reported to negatively affect the recovery of some analytes such as bentazone, bromoxynil, 2,4-DB and MCPB [24]. In another study, where polychlorinated biphenyls (PCB) have been extracted from sediment samples, that is rich in carbon content, the recoveries were found to drop with increase in carbon content [25]. Therefore, it is important to explore the influence of matrix through aging, on the efficiency of PLE as well, although it is believed to be less prone to matrix effect. The ultimate goal should focus on performing a more selective extraction by varying the extraction conditions in favor of the analytes compared to the matrix components and the simultaneous

achievement of quantitative extraction of the target analytes of interest [26].

SPLE method has been successfully developed and applied in our research group [27] for screening of OCPs in real samples collected from the Upper Awash Agro Industry Enterprises (UAAIE). However, the soil samples collected from this area are almost identical in most of their physical and chemical properties. For instance, analyses showed that a pH range of 8.5 - 9.0, textural class of clay and organic carbon ranging from 1.0 to 1.5. Soils with different physico-chemical properties have different effects on the adsorption of most pesticides, especially at higher concentration levels [6] [28]. Hence, it was anticipated that the application of SPLE might face limitation when other soil types collected from different geographical locations, are encountered. This was a driving force to explore on the efficiency of SPLE by spiking OCPs to various soil samples collected from different geographical locations in Ethiopia. This approach of checking for the exhaustiveness of the SPLE method was a unique approach. The aim of this study was therefore to determine whether the time that the OCPs remained in the various soil types affect the ease of their extraction in SPLE. Furthermore, it was to correlate the soil characteristics with the recovery determined using SPLE technique.

2. Materials and Methods

2.1. Chemicals and Materials

Acetone, *n*-hexane and *n*-heptane (Pestanal grade) were obtained from Riedel-de Haën, (Seelze, Germany). Florisil adsorbent (60 - 100 mesh), sodium sulfate anhydrous (puriss, analytical reagent grade $\geq 99\%$) and diatomaceous earth (acid washed and then calcined) were purchased from Whatman (Maidstone, UK). Individual standards of tetrachloro-*m*-xylene and decachlorobiphenyl were obtained from Dr. Ehrenstorfer, GmbH (Augsburg, Germany). Stock solutions of tetrachloro-*m*-xylene and decachlorobiphenyl were prepared at concentration levels of 75 and 66 $\text{mg}\cdot\text{L}^{-1}$ in *n*-hexane, respectively. Mixture of tetrachloro-*m*-xylene and decachlorobiphenyl ($0.5 \text{ mg}\cdot\text{L}^{-1}$) was prepared in *n*-hexane from the individual stock solution. This solution was used as internal standard (IS) throughout the study in which tetrachloro-*m*-xylene was used as time reference and decachlorobiphenyl as an IS for quantification purpose. Standard mixtures of 13 OCPs were purchased from AccuStandard Inc. (New Haven, CT, USA) as solutions, prepared in *n*-hexane:toluene (1:1, *v/v*); with concentration of 2 $\text{mg}\cdot\text{mL}^{-1}$. A seven-point calibration set of 13 OCPs was prepared in the concentration interval of 5 - 250 $\text{ng}\cdot\text{mL}^{-1}$. An internal standard mixture having, concentration of 33.33 $\text{ng}\cdot\text{mL}^{-1}$, was added into all calibration standards. The chemical structure of the OCPs studied and some of their physicochemical properties are provided in **Figure 1** and **Table 1**, respectively.

A Büchi rotary evaporator (Flawil, Switzerland) was used in the evaporation step. A nitrogen evaporator was also utilized whenever there was a need of reducing extracts to certain specific volumes. All glasswares used throughout the experiments were machine washed and then baked at 450°C for 12 h. They were

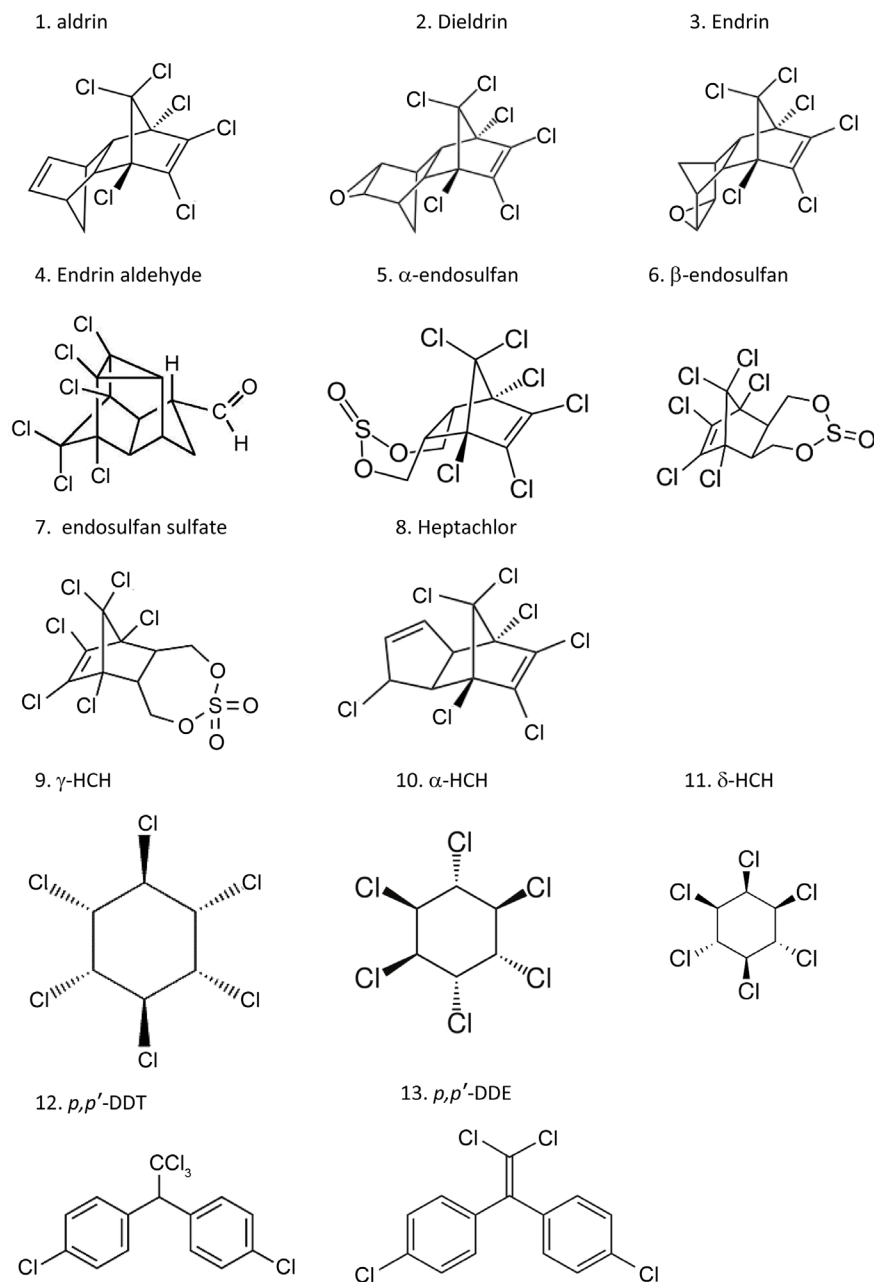


Figure 1. Chemical structure of the target OCPs.

further rinsed with *n*-heptane and acetone prior to their use.

2.2. Soils Used for Spiking

Four soil samples (Werrer, Genchi, Teppi and Nekemt soil) were obtained from Ethiopian National Soil Laboratory. They were collected from different parts of the country: Werrer soil (WS) from Afar region which is semi-arid area, Genchi soil (GS) from central high land, Teppi soil (TS) from south western Ethiopia, high rain fall area and Nekemt soil (NS) from somewhat moderate rain fall area, which were already ground and sieved through a 2-mm pore sieve and characterized, were obtained from Ethiopian National Soil Laboratory in Addis Ababa.

Table 1. Selected physicochemical properties of OCPs studied [27] [29] [30] [31].

OCPs	Physicochemical properties					
	Molecular mass (g·mol ⁻¹)	Water solubility (mg·L ⁻¹) at (°C)	Melting point (°C)	Log K _{ow}	Vapor pressure, mmHg; at (°C)	Henry's constant at 25°C (atm m ³ ·mol ⁻¹)
Alpha-HCH	290.83	69.5 (28°C)	159 - 160	3.8	4.5 × 10 ⁻⁵ (25°C)	6.86 × 10 ⁻⁶
Gamma-HCH	290.83	7.3 (25°C)	112.5 - 113.5	3.78	4.5 × 10 ⁻⁵ (20°C)	3.5 × 10 ⁻⁶
Heptachlor	373.3	0.056 (25°C - 29°C)	95 - 96	3.9	3.7 × 10 ⁻⁴ (25°C)	2.62 × 10 ⁻³
Delta-HCH	290.83	10.0 (25°C)	141 - 142	4.14	3.5 × 10 ⁻⁵ (25°C)	2.1 × 10 ⁻⁷
Aldrin	364.91	0.011 (20°C)	104 - 105.5	6.5	1.28 × 10 ⁻⁴ (25°C)	4.9 × 10 ⁻⁵
Alpha-endosulfan	406.9	0.32 (22°C)	109.2	3.83	9 × 10 ⁻³ (80°C)	1.5 × 10 ⁻⁵
pp' DDE	318.03	0.12 (25°C)	89	6.0	6 × 10 ⁻⁶ (25°C)	2.1 × 10 ⁻⁵
Dieldrin	380.91	0.11 (25°C)	176 - 177	6.2	5.89 × 10 ⁻⁶ (25°C)	5.2 × 10 ⁻⁶
Endrin	380.9	0.2 (25°C)	235	5.45	2 × 10 ⁻⁷ (25°C)	4 × 10 ⁻⁷
pp' DDT	354.49	insoluble	108.5 - 109	6.79	2 × 10 ⁻⁷ (20°C)	8.3 × 10 ⁻⁶
Beta-endosulfan	406.9	0.33 (22°C)	213.3	3.52	9 × 10 ⁻⁶ m (80°C)	1.91 × 10 ⁻⁵
Endrin aldehyde	381.9	50 (25°C)	145 - 149	4.7	2 × 10 ⁻⁹ (25°C)	2 × 10 ⁻⁹
Endosulfan sulfate	422.92	0.22 (22°C)	181	3.66	N/A	2.61 × 10 ⁻⁵

Geographical locations of the sampling areas are as follows: Teppi is located at latitude of 7°11'51.89"N and longitude of 35°25'44.6"E with elevation of 1198.8 m above sea level; Werrer (Afar), at latitude of 11°45'01.83"N and longitude of 40°57'31.28"E with elevation of 447.1 m above sea level; Nekemt, at altitude of 9°05'22.49"N and longitude 36°33'27.62"E with elevation of 1127.5 m above sea level; and Ginchi, at altitude of 9°02'10.65"N and longitude 38°08'36.41"E with elevation of 2240.3 m above sea level. Soil samples were commonly taken from a maximum of 25 cm depth following the procedure described by Westbom *et al.* [27]. Physico-chemical properties of the soil samples used in the present investigation are given in **Table 2**.

Additionally, two clay soil samples, namely; red Gullale clay (RGC) and yellow Gullale clay (YGC) were collected from Burayyu Brick Factory compound located at Gullale subcity, Western Addis Ababa, and also used for the investigation. Both clay samples were ground in a mortar with a pestle and sieved through a 2-mm pore sieve in our laboratory.

2.3. Target Analytes Spiking

A spiking solution having a concentration of 1 mg·L⁻¹ (containing a mixture of 13 OCPs) was prepared in *n*-hexane by diluting the intermediate stock solution (10 mg·L⁻¹). The soil aliquot (100 g) from each of the six samples was taken into a 250 mL Teflon capped bottle. The slurry method of spiking was used for preparing fortified soil samples [32] [33]. In the method, 100 mL of acetone was added in order to completely immerse the soil, followed by 5 mL of the spiking solution, which corresponds to a spiking level of 50 ng·g⁻¹ soils. All the samples were tightly capped and then shaken at a speed of 200 rpm for four hours using

Table 2. Physical and chemical properties of the soil samples.

Soil type	pH (H ₂ O) (1:2.5)	EC	Organic matter composition (%)	Texture (%)		
				Slit	Clay	Sand
WS	8.2	0.166	1.08	14	44	42
GS	6.5	0.015	2.53	13	29	58
TS	6.3	0.026	3.62	22	32	46
NS	5.3	0.009	2.55	20	38	42

orbital shaker. Furthermore, they were intermittently shaken manually every 40 min to ensure homogeneous distribution of the spiked OCPs. After removing the cap from the bottles, all samples were loosely covered with perforated aluminum foil and kept in a fume hood until complete evaporation of acetone. The OCPs were aged in the soil samples for a total period of 9 weeks in the fume hood.

2.4. Extraction of OCPs

Analytes extractions were performed on an ASE 300 system (Dionex, Sunnyvale, CA, USA). Extractions were carried out on the fortified soil samples using SPLE method developed earlier [19]. First round extraction was performed after one week of aging time and the second after nine weeks. In both rounds, 2 g aliquot of each fortified soil sample was taken separately in triplicates. Each sample was mixed with 4 g sodium sulphate, used as a drying agent, and then ground in a mortar with a pestle. The homogenized sample was quantitatively transferred into the extraction cell by rinsing the mortar and pestle with a small amount of sodium sulfate powder. The cell packing was carried out as described earlier [19] and the same PLE parameters have also been used in the present study. These include a temperature of 100°C, 3 × 10 min static time, extraction solvent: acetone/*n*-heptane, heat-up time of 5 - 8 min, a flush volume of 50%, a purging time of 60 s, a pressure of 10.3 MPa and 34 mL extraction cells.

A total of 36 extracts were collected from the two stages of extractions. IS was immediately added (100 µL) into each collection bottle of the PLE extract. The extracts were concentrated to about 1 mL using a rotary evaporator, and then quantitatively transferred to a GC-vial with *n*-heptane resulting in the final volume of approximately 1.5 mL.

2.5. Gas Chromatography

A dual column gas chromatograph model GC 6890N (Agilent Technologies Inc., Palo Alto, CA, USA) equipped with two ⁶³Ni-µECDs and a 7683 series autosampler/injector (Agilent) was used for quantitative analysis. Sample aliquots were analysed by injecting 1 µL of each sample on-column into the GC. The dual-column system utilized for separation of the analytes was a HP-5 ms column (Agilent) coupled in series to a HT-5 column (SGE Analytical Science Pty Ltd., Ringwood, Australia) and a parallel DB-17 column (Agilent). Parallel columns were coupled to the inlet via a deactivated retention gap (Agilent) using a

quick-seal glass “T”. The temperature program consisted of an initial 2 min hold at 90°C and then ramped at 50°C·min⁻¹ to 150°C and retained for 1 min. Thereafter, the temperature was increased with 7°C·min⁻¹ to 280°C, where it was finally held for 30 min, giving a total run time of 52.77 min. Quantification was made by means of peak height measurement (the detector giving the lowest signal was selected) using the ChemStation software (Agilent) and for statistical significant tests, one way ANOVA was applied using Microsoft excel 2007.

3. Results and Discussion

3.1. Effect of Aging in the Four Soil Samples

To investigate the influence of the time elapsed between spiking and extraction, *i.e.*, contact time or aging, extraction was performed in one week and nine weeks time after spiking. The extraction recoveries obtained are shown in **Table 3**. The results were highly reproducible as manifested by very low SDs.

Table 3. Percent recoveries obtained after aging OCPs in the four soil samples.

Analyte	Aging time in week (s)	Extractability, % Recovery (SD) [*] , of the analytes from the soil samples			
		TS	NS	WS	GS
alpha-HCH	1	120.6 (0.8)	120.4 (0.1)	107.7 (1.5)	116.3 (1.6)
	9	105.1 (0.9)	114.5 (0.7)	100.0 (2.7)	101.0 (0.1)
gamma-HCH	1	117.6 (1.9)	116.8 (1.0)	108.0 (1.9)	114.8 (1.8)
	9	103.3 (0.4)	109.5 (0.6)	100.8 (3.2)	99.1 (0.2)
Heptachlor	1	112.0 (0.8)	112.5 (0.3)	106.6 (2.9)	111.3 (1.2)
	9	103.9 (0.5)	95.4 (0.2)	94.0 (2.0)	98.1 (1.4)
delta-HCH	1	129.3 (0.7)	128.5 (0.3)	119.2 (3.0)	125.1 (3.0)
	9	119.4 (0.7)	123.8 (0.8)	106.3 (3.6)	109.3 (1.3)
Aldrin	1	74.8 (0.5)	68.0 (0.4)	62.4 (1.0)	76.9 (0.9)
	9	65.0 (0.9)	76.6 (1.2)	73.7 (2.1)	69.4 (0.3)
alpha-endosulfan	1	86.6 (0.8)	88.3 (0.6)	93.5 (1.5)	85.2 (2.1)
	9	18.0 (0.1)	55.3 (0.2)	14.3 (0.5)	61.9 (0.3)
pp' DDE	1	118.5 (0.9)	116.7 (1.0)	108.0 (2.2)	112.6 (2.8)
	9	109.4 (0.5)	110.9 (0.6)	101.9 (3.4)	98.3 (0.8)
Dieldrin	1	89.7 (1.0)	92.4 (0.8)	85.4 (2.2)	87.6 (0.6)
	9	85.9 (0.5)	90.5 (1.6)	79.2 (3.7)	78.0 (1.4)
Endrin	1	120.7 (0.6)	119.0 (1.2)	116.3 (2.8)	120.5 (2.0)
	9	115.2 (0.4)	114.2 (0.8)	109.1 (3.2)	103.8 (0.4)
pp'-DDT	1	108.7 (1.9)	112.5 (1.3)	107.3 (1.2)	112.9 (2.5)
	9	116.1 (0.5)	114.6 (1.1)	105.3 (3.0)	105.6 (0.4)
beta-endosulfan	1	91.9 (1.5)	93.4 (0.7)	119.4 (2.9)	92.1 (2.4)
	9	62.9 (0.1)	84.1 (0.2)	50.2 (2.0)	78.3 (0.02)
Endrin aldehyde	1	28.9 (5.8)	57.4 (4.1)	53.4 (2.7)	50.9 (1.1)
	9	4.2 (0.5)	5.1 (0.3)	5.0 (0.4)	5.7 (1.7)
Endosulfan sulfate	1	95.5 (1.2)	93.4 (1.0)	195.9 (4.1)	95.3 (2.0)
	9	82.6 (0.6)	84.1 (0.2)	173.4 (8.3)	80.3 (1.3)

*standard deviation for triplicate measurements.

Although background interference may affect recoveries $\leq 100\%$, it is usually not suspected unless recoveries go beyond 100%. Therefore, unfortified soil samples were used to assess whether peaks due to naturally occurring organic compounds extracted from the soil samples would interfere with the analyte peaks. Based on the highest signal obtained from one of the two ECD detectors, background interferences were calculated for each analytes in the soil samples. In most of the cases the chromatograms of the unspiked soil extracts showed less than 5% background interferences at the retention time of the target analytes. Considerable interferences were observed in WS soil. These were 13, 14, 33, 39, and 108% for α -endosulfan, *p,p'*-DDE, β -endosulfan, endrin aldehyde and endosulfan sulphate, respectively. Background interference contributed 42 and 11% of the recovery obtained for α -HCH in TS and β -endosulfan in NS, respectively. An interfering peak that co-elutes with endosulfan sulfate is responsible for the unrealistically high recovery (196%) of endosulfan sulfate in WS soil (Table 3).

Attributing inflated recoveries to the background interferences, a real recovery of about 100% can be assumed for most of the OCPs regardless of the aging time. However, after 9 weeks of aging, the recoveries of α -endosulfan and endrin aldehyde were considerably reduced in all the soil samples. This may most likely be attributed to the evaporation losses and microbial degradation in the soil. It is known that α -endosulfan degrades by the soil microorganisms [34] [35]. No studies on the environmental fate of endrin aldehyde could be found in the available literature [36]. Limited information on the physical and/or chemical properties of endrin aldehyde indicates that it is highly immobile in the soil and will not volatilize significantly from soil [36]. This is in contrast to the results obtained in the present study.

The overall results for most of the OCPs by the SPLE method suggest a satisfactory efficiency of the extraction method under the experimental conditions set. Furthermore, one-way ANOVA was applied to test whether aging leads to significant differences between the mean values obtained. Hexacyclohexane and diphenyl aliphatic OCPs in WS and all OCPs in GS (except for endrin aldehyde and α -endosulfan) did not show statistically significant differences in recovery which is symptomatic of the efficiency of SPLE method to extract the aged OCPs from the soil. On the other hand, statistically significant differences were observed for all OCPs in TS, for most OCPs in NS (except for endrin, dieldrin and DDT) and for cyclodiene OCPs in WS (except for endrin, dieldrin and endosulfan sulfate). Nevertheless, the recovery after nine weeks of aging time is still very good in all the soil samples which also implies the efficiency of the SPLE method.

3.2. Quality Assurance

Quality and reliability of the data generated by a given method could be assured employing various parameters including the limit of detection (LOD) and limit of quantitation (LOQ). LOD of the analyte may be described as that concentra-

tion which gives an instrument signal significantly different from the “blank” or “background” signal [37] while LOQ is the lowest concentration level at which a measurement is quantitatively meaningful [38].

In this work, the LOD and LOQ were established for each target analyte by performing triplicate extractions and analyses on each blank soil sample (without spiking). Then, 3 and 10 times standard deviation of the blank (S/N) were reported as LOD and LOQ, respectively [39] [40]. The results obtained are shown in **Table 4**. As it can be seen from **Table 3**, for all soils and clays the amount spiked was $50 \text{ ng}\cdot\text{g}^{-1}$, the smallest recoveries were observed for α -endosulfan and endrin aldehyde after 9 weeks of aging. For instance, the percent recovery of endrin aldehyde for TS soil (9 weeks of aging) was 4.2% (**Table 3**). This corresponds to $2.1 \text{ ng}\cdot\text{g}^{-1}$ which is much higher than both the LOD ($0.328 \text{ ng}\cdot\text{g}^{-1}$) and LOQ ($1.092 \text{ ng}\cdot\text{g}^{-1}$) values of endrin aldehyde (**Table 4**). Similarly, percent recovery of α -endosulfan in YGC (9 weeks of aging) was 1.6 (**Figure 2**). It corresponds to $0.817 \text{ ng}\cdot\text{g}^{-1}$, which is also significantly higher than both the LOD ($0.002 \text{ ng}\cdot\text{g}^{-1}$) and LOQ ($0.006 \text{ ng}\cdot\text{g}^{-1}$) values. Thus, it could be concluded that the results obtained are remarkably different from the blank, ensuring reliability of the proposed analytical method.

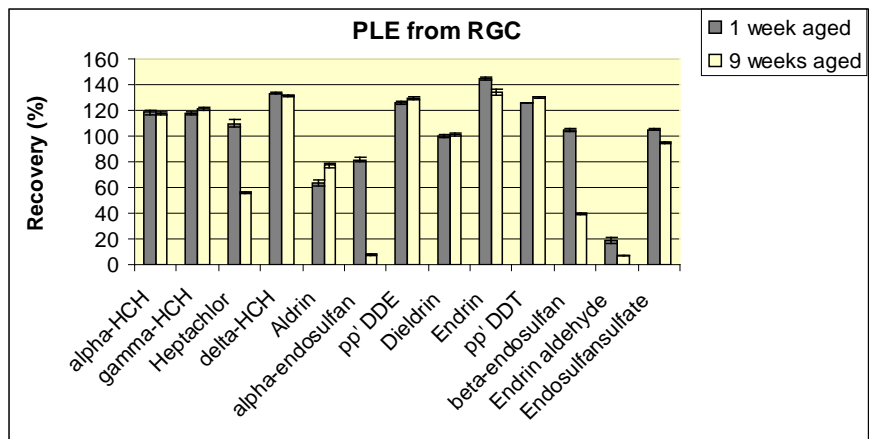
3.3. Effect of Aging in the Two Clay Soils

The results obtained from the two clay soil samples that were similarly spiked under the same experimental conditions as that of the four soil types are shown in **Figure 2**.

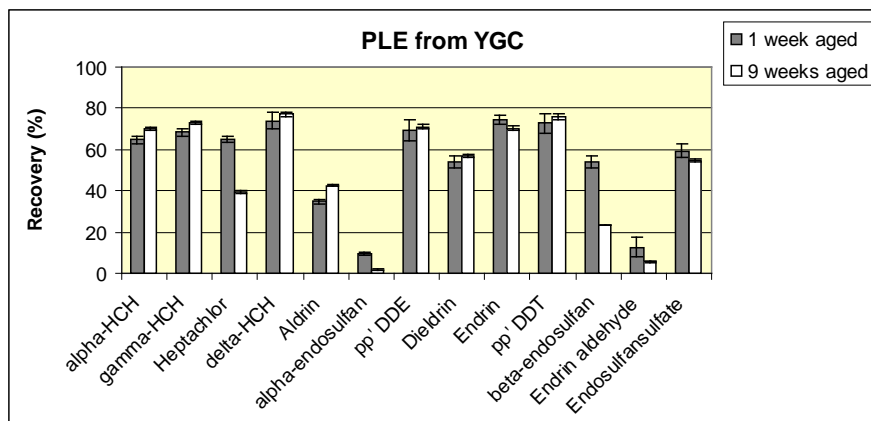
There is considerable difference between recoveries obtained from RGC and

Table 4. Limit of detection (LOD) and limit of quantification (LOQ), in each soil sample, for the target analytes studied.

Analytes	LOD and LOQ ($\text{ng}\cdot\text{g}^{-1}$)											
	TS		NS		WS		GS		RGC		YGC	
	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ
alpha-HCH	3.332	11.108	0.006	0.020	0.005	0.016	0.004	0.012	0.001	0.005	0.098	0.327
gamma-HCH	0.765	2.550	0.310	1.033	0.174	0.578	0.151	0.503	0.094	0.312	0.060	0.201
Heptachlor	0.319	1.063	0.180	0.601	0.328	1.095	0.100	0.334	0.303	1.010	0.186	0.619
delta-HCH	0.710	2.367	0.118	0.394	0.027	0.090	0.498	1.659	0.320	1.066	0.141	0.471
Aldrin	0.546	1.821	0.006	0.020	0.290	0.965	0.017	0.057	0.878	2.927	0.002	0.008
alpha-endosulfan	0.504	1.681	0.180	0.599	1.194	3.981	0.002	0.006	0.281	0.937	0.002	0.006
pp' DDE	0.586	1.954	0.377	1.257	0.295	0.984	0.027	0.089	0.061	0.203	0.496	1.652
Dieldrin	0.525	1.750	0.539	1.797	0.064	0.212	0.134	0.448	0.178	0.594	0.168	0.560
Endrin	0.700	2.333	0.544	1.814	0.513	1.709	0.515	1.716	0.155	0.515	0.281	0.938
pp' DDT	0.352	1.174	0.129	0.431	0.182	0.605	0.388	1.294	0.741	2.470	0.182	0.605
beta-endosulfan	0.322	1.073	0.440	1.467	0.388	1.294	0.197	0.656	1.382	4.605	0.384	1.279
Endrin aldehyde	0.328	1.092	0.003	0.011	0.685	2.283	0.347	1.157	0.003	0.011	0.154	0.512
Endosulfan Sulfate	0.179	0.598	0.154	0.512	4.492	14.974	0.734	2.446	0.309	1.029	0.072	0.240



(a)



(b)

Figure 2. Recoveries of OPCs spiked on red Gulale clay (a) and yellow Gulale clay (b).

YGC samples. As can be seen in **Figure 2**, recovery $\geq 100\%$ was achieved for most OCPs from RGC clay sample, which is quite similar with the recoveries from the four soil samples (TS, NS, WS, and GS). In contrast, a recovery $\leq 75\%$ was obtained in the extraction of the OCPs aged in YGC. Obviously, this may indicate the existence of strong interaction between the OCPs and the components of YGC. The most persistent complexes result from direct covalent binding of pesticides to the soil humic matter or clay [19] [41]. Humic substances are amorphous, dark-coloured organic compounds which are relatively resistant to chemical and biological degradation [42] [43]. As can be seen from chemical structure of the studied OCPs (**Figure 1**), it is possible to think of strong covalent binding to occur and take place via the polar functionalities on the OCPs to the components of YGC. Consequently, the analytes remained bound in the soil matrix and hence become more resistant to extraction. Furthermore, such interaction may also decrease bioavailability, biodegradation and bioremediation of the pesticides. A decrease in bioavailability is a desired property in that it makes the OCPs less accessible to the non-target organisms.

YGC could have a potential application in Ethiopian situation, where there is still considerable scarcity of pure drinking water, where water bodies like Awash

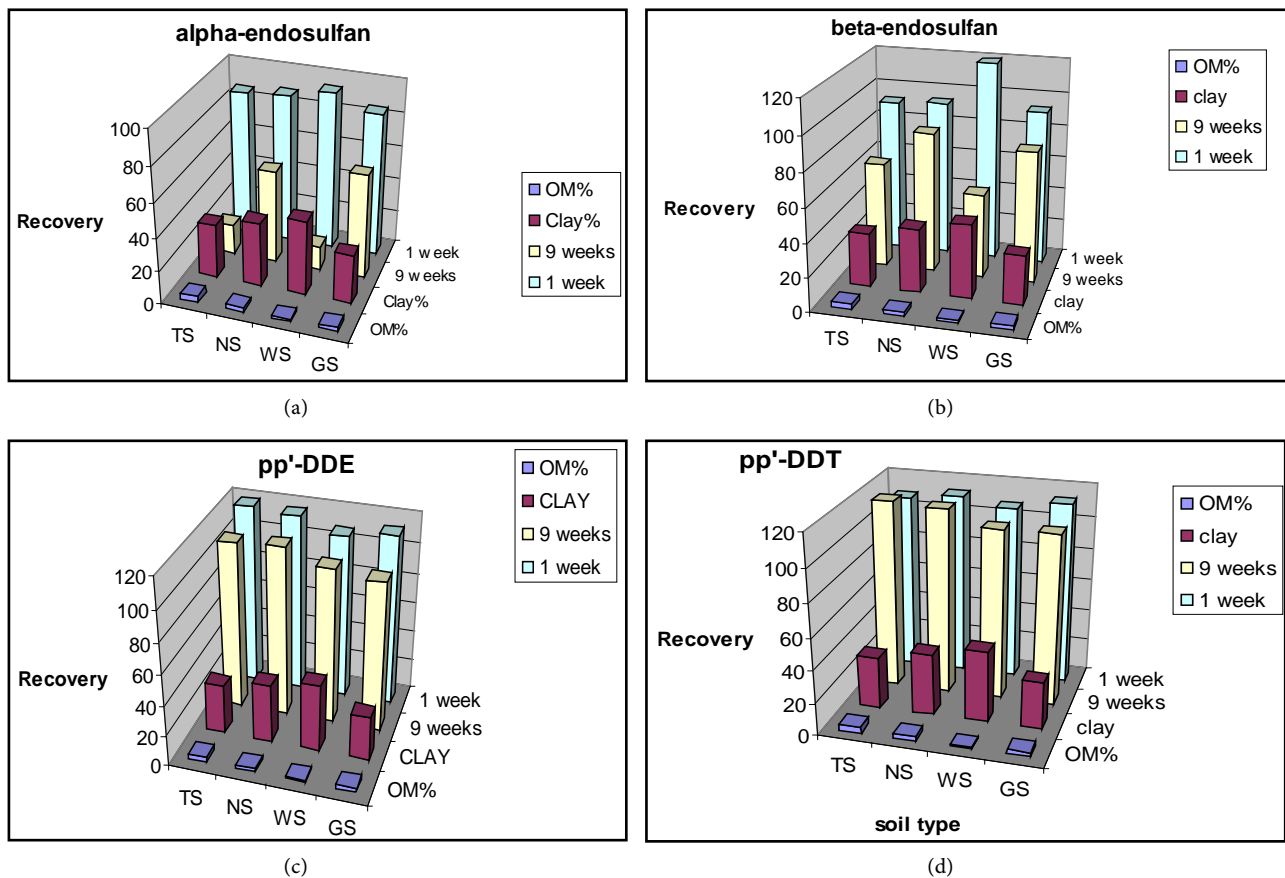


Figure 3. Soil characteristics and extractability comparisons for α -endosulfan (a), β -endosulfan (b), p,p' -DDE (c) and p,p' -DDT (d).

River is highly vulnerable to pesticide pollution. In the countryside, people travel long distances to fetch drinking water and at home keep in pots that are made from clay soils. If house hold utensils, used as water containers in the rural areas, are made from YGC soil, it could bound the pollutants and remarkably reduce their toxic effect by hindering mobility (sequestration). YGC seems very promising to mitigate pollution risks in rural areas of the countries, like Ethiopia, where there is a limited access to pure drinking water.

Furthermore, YGC could also possibly be used in pesticide formulation industries. Renewed attention is being directed to designing less hazardous, sustainable formulations, such as controlled-release (CR) formulations, which supply the active ingredient (AI) gradually over time, thereby decreasing the risk of off-site movement of highly mobile pesticides [44]. Clay minerals were suggested long ago as pesticide carriers in CR formulations mainly because of their attractiveness in terms of economy and sustainability [40]. Currently, new designs of pesticide formulations on the basis of surface-modified clay minerals are being proposed to improve the affinity of clay minerals for selected pesticides and to control the desorption rate once added to the environment [44] [45]. It is hoped that the YGC soil could also have a potential application for preparation of CR formulations. It is therefore a recommendation from this study to initiate

a research project to explore how YGC soil could be used, on a wider scale by the local people, to characterize and optimize the binding of OCPs and other pesticides in the YGC soil.

3.4. Correlation between the Soil Characteristics and Extractability of OCPs

Characteristics that might affect release of OCPs from the soil matrix include organic matter content, type and content of clay, physical and chemical property of the target analytes and how long the target analytes remained in the soil. Three dimensional diagrams are shown in **Figure 3** for some of the OCPs studied to look for any correlation that might exist between the soil characteristics (organic matter and clay content) and the recovery obtained.

As can be seen in **Figure 3**, in spite of the difference in OM and clay percentage between the TS and WS soils, comparable recoveries were observed for α -endosulfan, β -endosulfan, *p,p'*-DDE, and *p,p'*-DDT. The same holds true for the remaining OCPs studied. Soil organic matter is known to be an important parameter affecting analyte recovery. The larger the organic matter content, the greater will be the adsorption of pesticides [1] [7] [46] [47]. There are frequent reports in the literature describing that adsorption of pesticides are not solely related to either the organic matter content or the clay content although it appears to be positively correlated with both of these soil components [48] [49] [50] [51].

It is important to note that a great extent of adsorption doesn't necessarily mean that the recovery is low. Indeed, this is determined by exhaustiveness of the extraction method employed. If the extraction method is efficient in recovering both the analytes that are "tightly" or "loosely" bound to the matrix, it is unlikely to see a difference in the ultimate recovery achieved. In the present study, there is no apparent correlation between extractability and the characteristics of the soil samples studied suggesting that the SPLE methodology is efficient for exhaustive extraction of the OCPs from the soil samples. However, it is very important to reoptimize extraction parameters whenever the soil samples like YGC are employed. Perhaps, the other reason for the absence of clear correlation could probably be that there is no big difference in the clay and OM contents of the studied soils which is perceptible as displayed in **Figure 3**, *i.e.*, capable of causing recognizable effect on efficiency. As a support to the above suggestion, two way ANOVA analysis also revealed that it is rather the aging that caused statistically significant effect on the recoveries than the soil type.

Representative chromatograms in one of the selected soil matrices, *i.e.*, yellow Gullele clay (YGC), are shown in **Figure 4**; after aging the target analytes in the clay sample for one week (a), for nine weeks (b), at zero time or spiking standard solution (c) and the standard blank (d).

4. Conclusions

In summary organic matter content, type and content of clay, physical and

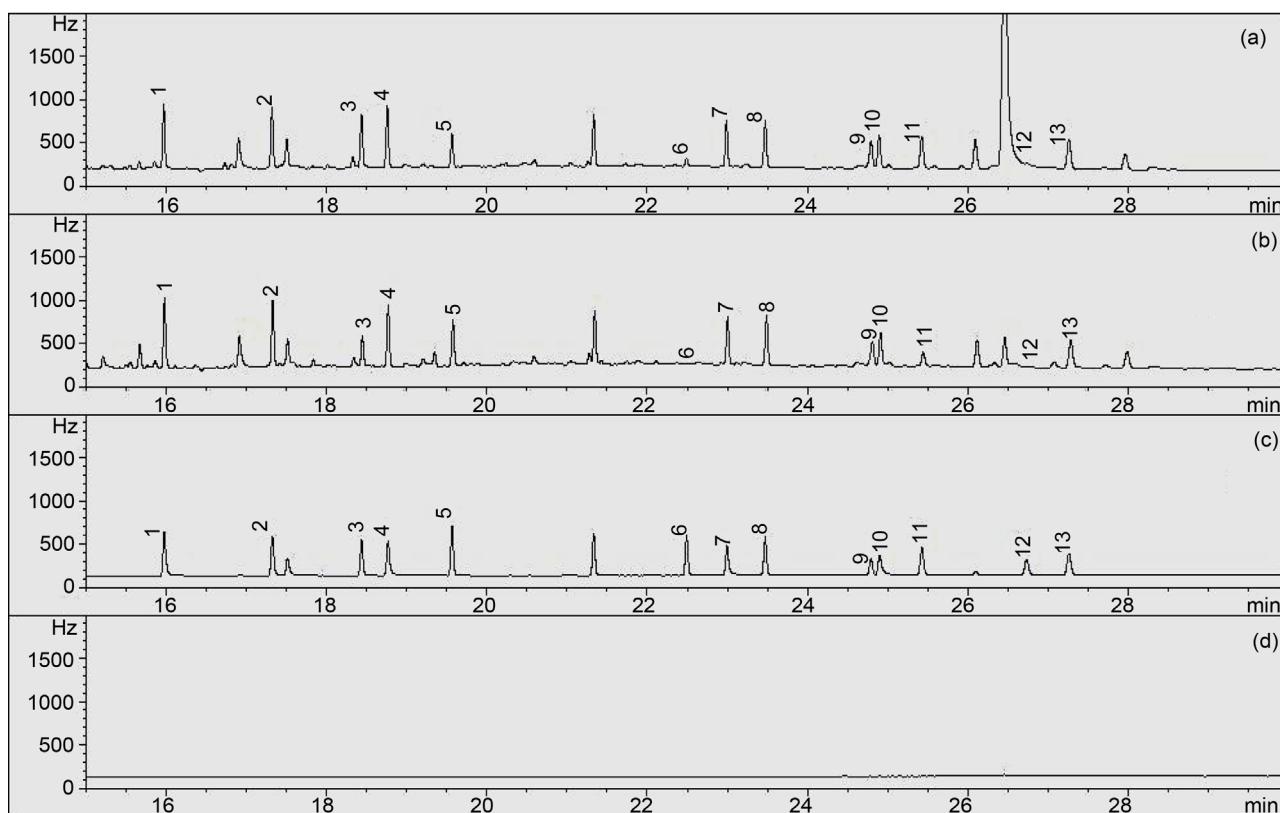


Figure 4. Typical Chromatogram: (a) YGC after one week aged (b) YGC after nine weeks aged (c) standard solution used for spiking set at time zero (d) blank *n*-heptane. Identification of peaks: 1. alpha-HCH (Rt-16.01 min) 2. gamma-HCH (Rt-17.35 min) 3. Heptachlor (Rt-18.47 min) 4. delta-HCH (Rt-18.80 min) 5. Aldrin (Rt-19.60 min) 6. alpha-endosulfan (Rt-22.52 min) 7. pp' DDE (Rt-23.02 min) 8. Dieldrin (Rt-23.50 min) 9. Endrin (Rt-24.82 min) 10. pp'-DDT (Rt-24.92 min) 11. beta-endosulfan (Rt-25.46 min) 12. Endrin aldehyde (Rt-26.76 min) 13. Endosulfan sulfate (Rt-27.29 min).

chemical properties of the target analytes and how long these analytes remained in the soil are the major factors to be considered in the evaluation of extraction efficiency. In this study, aging and type of clay are observed to be the major factors. SPLE has been demonstrated to be an efficient method in five of the soil samples investigated. However, recovery was considerably minimized in the case of YGC, which proves the hypothesis of the experiment that efficiency of SPLE is matrix dependent. Therefore, it is unlikely to come up with a single multi-residue exhaustive extraction method that works uniformly for all types of the soil matrices. This emphasizes the importance of optimizing the extraction parameters due to distinct properties of the analyte-matrix interactions. From the findings of the current study, there are promising indications for the use of the YGC in the mitigation of the OCPS contamination risks and thus further investigations could be continued in order to explore and establish conditions for its use particularly in the rural areas of countries, like Ethiopia, where treated and pure drinking waters are scarce.

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